Synthesis and Study of New Cyclometallated Complexes

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CONTENTS

ABBREVIATIONS

acacH	acetylacetone (2,4-pentanedione)
bacH	benzoylacetone (1-phenyl-1,3-butanedione)
bipy	2,2'-bipyridine
CIS	coordination induced shift
COSY	correlation spectroscopy
cp	cyclopentadienide
dbmH	dibenzoylmethane (1,3-diphenyl-1,3-propanedione)
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
eq.	molar equivalent
HMQC	heteronuclear multiple-quantum coherence
IR	infra red
Mp	melting point
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
TBAH	tetrabutylammonium hydroxide
terpy	2,2':6',2''-terpyridine
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TOCSY	total correlation spectroscopy

ABSTRACT

Twenty-nine heteroaromatic ligands, which are potentially capable of forming cyclometallated complexes, have been reacted with palladium and rhodium salts. In addition to a number of mono-cyclometallated complexes, two doubly cyclopalladated complexes have been prepared, as have a number of coordination complexes.

Specifically, a number of phenoxy- and phenylthio-substituted pyridines and diazines, four of which could potentially be doubly cyclometallated, have been synthesised, and their coordination and cyclopalladation chemistry investigated. The previously reported reactions of 2-benzoylpyridine with rhodium trichloride trihydrate have been revisited, and are discussed in relation to the formation and characterisation of a novel cyclorhodated complex of the ligand. The syntheses—*via* homo-coupling reactions of aryl halide precursors—and cyclopalladations of two structural analogues of 2,2':4',4":2",2"'-quaterpyridine are also described.

All of the soluble complexes and ligands have been fully characterised by ^{1}H and ^{13}C NMR, using combinations of various one- and two-dimensional NMR techniques. The trends in the coordination induced shifts, observed for the NMR spectra of a series of cyclopalladated acetylacetonate complexes and the corresponding free ligands, are discussed, as are those for a related series of octahedral cyclorhodated complexes. Other methods, including IR spectroscopy, mass spectrometry and elemental analysis, have been used to characterise the prepared complexes. In addition, the characterisation of three cyclometallated complexes and four coordination complexes, by single crystal X-ray structure determination, is described.

Introduction

INTRODUCTION

Cyclometallated complexes (also called organometallic intramolecular-coordination complexes) are defined as those complexes in which a ligand has undergone "an intramolecular metallation with the formation of a chelate ring containing a metal-carbon σ bond".[1] Thus, cyclometallated complexes incorporate multidentate ligands in which one of the coordinating atoms is carbon, and may be conveniently represented by a general structure (figure 1).[2]

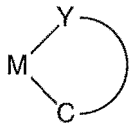
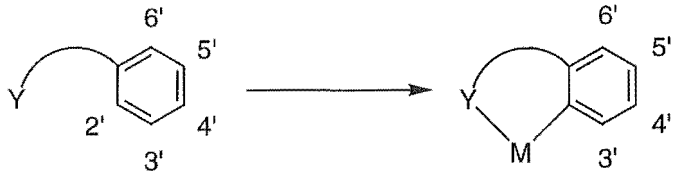


Figure 1

Such complexes were first described as "Metallorganische Innerkomplexe" by Bähr and Müller in 1955[3] and are characterised by the presence of a Y-M-C cyclic system in which Y represents a coordinating donor (Lewis base) that is directly connected by the ligand structure to the metallated carbon atom. Given that this cyclic system includes a donor-metal bond—characteristic of coordination complexes—and a carbon-metal bond—characteristic of organometallic complexes—cyclometallated complexes, the term introduced by Trofimenko in 1973,[4] represent the interface between coordination and organometallic chemistry.[5] Complexes of this type have been the subject of ongoing interest, both from theoretical and applied perspectives, many reviews[1,5-19] and a monograph[20] having been published.

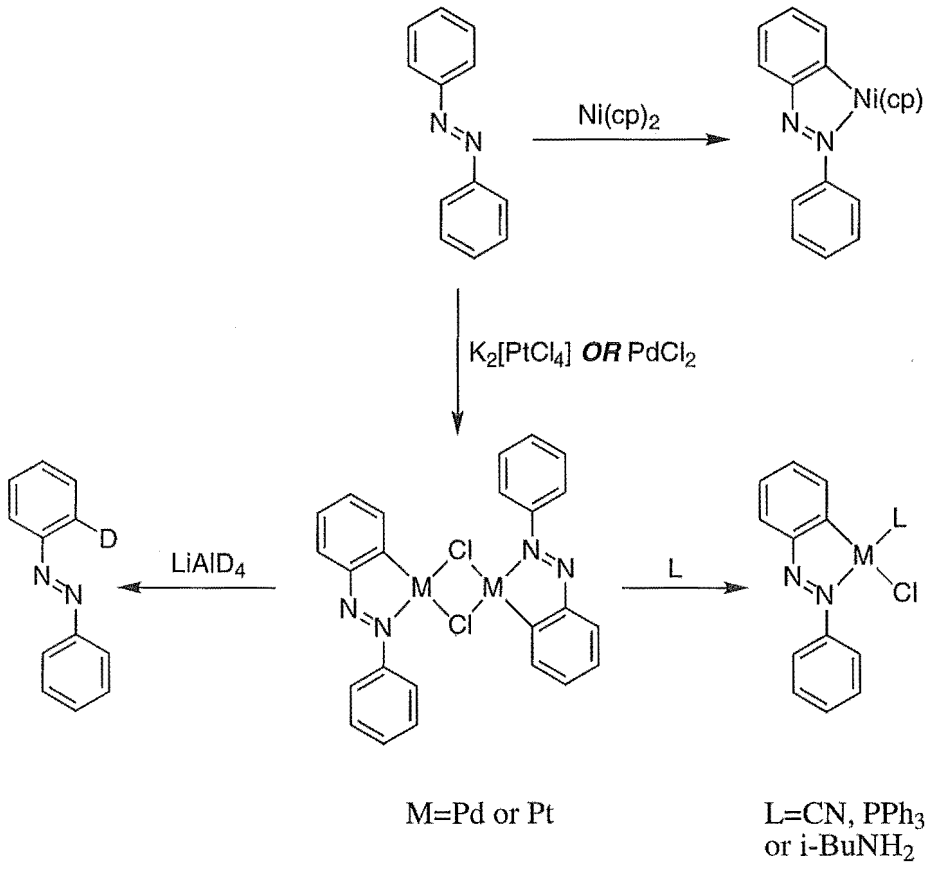
For the general structure shown above (figure 1), an individual cyclometallated complex can be categorised according to: the type of carbon atom (aliphatic, aromatic *etc.*); the coordinating Lewis base, Y; the choice of metal, M; and the size of the chelate ring. Within this classification of cyclometallated complexes is the distinct category of orthometallated complexes, named as such because the metallation has occurred selectively at the *ortho* position of an aromatic system (scheme 1). The majority of reported cyclometallations are orthometallations,[20] and it is such reactions, leading to

the activation of an aryl carbon-hydrogen bond, which are of prime interest within this thesis.



Scheme 1*

The first orthometallated complex, formed upon reaction of azobenzene and nickelocene, was reported in 1963 by Kleiman and Dubeck (scheme 2).[21] The position of bonding between the phenyl ring and the nickel was reported, on the basis of steric considerations, to be *ortho* to the azo group.[21]



Scheme 2

Two years later, Cope and Siekman reported that reaction of azobenzene with potassium tetrachloroplatinate or palladium dichloride gives chloro-bridged dimeric

*Note that the numbering of the cyclometallated phenyl ring is the same in the complex as in the free ligand. Whilst this leads to non-standard numbering within the complex, this system is adopted throughout this thesis to permit easy comparison, when considering NMR spectra, between the spectra of equivalent positions in the complexes and the corresponding free ligands.

complexes (scheme 2).[22] Upon treatment with cyanide, phosphines or amines, these compounds do not release the free ligand but give new mononuclear complexes, which are cleavage products of the chloro-bridged dimers (scheme 2).[22] The authors determined the presence of a bond between the metal atom and the *ortho* carbon of the azobenzene ligand by decomposition of the chloro-bridged complexes with lithium aluminium deuteride. Hydrolysis of the reaction mixture with D_2O, followed by oxidation with air or mercuric oxide, gave azobenzene which was found to contain 4% d_0, 93% d_1 and 3% d_2 species (scheme 2). Comparison of the ^1H NMR spectrum of the resultant d_1-azobenzene with that of an authentic sample of the mono-*ortho*-deuterated compound showed that the two compounds were identical, thus establishing the position of metallation.[22]

The coordinating atom, Y, can be either σ or π bonded to the metal centre. In σ-coordinated complexes, which are the focus of this thesis, the donor atom represents nitrogen, phosphorus, arsenic and antimony in Group VA, oxygen and sulfur in Group VIA and chlorine, bromine and iodine in Group VII; however it is usually restricted to nitrogen, phosphorus, oxygen and sulfur.[20] The cyclometallations described in this thesis are of ligands which incorporate a nitrogen-containing heterocycle (figure 2); thus the donor atom is limited to nitrogen.

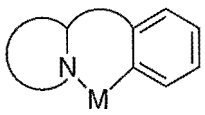


Figure 2

The first report of a cyclometallated complex incorporating a nitrogen-containing heterocycle was some thirty years ago.[23] Kasahara reacted sodium tetrachloropalladate with 2-phenylpyridine and with 2-phenylquinoline, and obtained the corresponding cyclopalladated chloro-bridged dimers. The position of the palladium-carbon bond was confirmed by deuteration experiments, analogous to those performed by Cope and Siekman (*vide supra*).

Returning to the more general definition of cyclometallated complexes, represented by figure 1, two variables remain to be discussed: the nature of the metal,

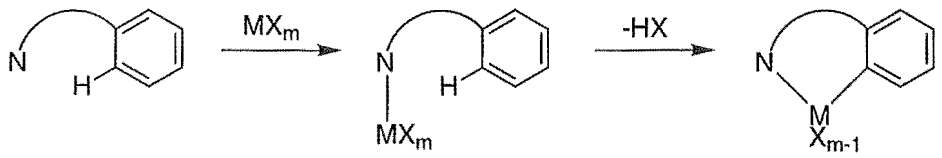
M; and the size of the metallocycle. A variety of metals have been incorporated into metallocycles formed either by direct reaction of the ligand with a metal precursor or by transmetallation reactions. The majority of reported complexes, however, include the middle transition metals, particularly those in Group VIII. Much of the published research has been done with palladium and platinum, because of the relative ease with which cyclometallation occurs with these metals and the stability of the complexes so formed. The work herein described is restricted to complexes in which M = Pd[24,25] or Rh,[26,27] that is cyclopalladated and cyclorhodated complexes. The first cyclorhodation was reported in 1969[28] followed, two years later, by the first cyclorhodation of a ligand which incorporates a nitrogen-containing heterocycle.[29]

Whilst an exhaustive survey of all the other different metals that have been incorporated into such complexes is beyond the scope of this introduction, those of particular note include: gold;[30] iridium;[31] manganese;[32] mercury;[33] and ruthenium.[34]

The ring size of the metallocycle formed upon cyclometallation is dependent on the choice of metal and on the structure of the ligand. The formation of five-membered metallocycles is most often reported, paralleling the observation that, for coordination complexes, ligands which form five-membered chelate rings give the most stable products.[20] Six-membered metallocycles are the most commonly observed of the other ring sizes, but reports of structures of this type remain comparatively rare.[35] Despite this, the metallocyclic ring sizes reported range from three-membered to nine-membered.[14,20]

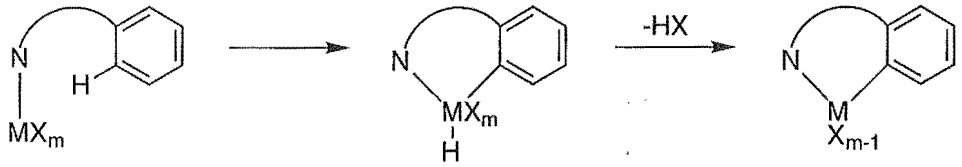
Cyclo- and ortho-metallation reactions result in the selective activation of a carbon-hydrogen bond. The complexes are generally produced by a reaction involving a two step mechanism (scheme 3).[20] The initial step is coordination of the Y donor group or atom—for the work described herein this a nitrogen lone pair—and the second step is cyclisation *via* electrophilic attack on the proximately situated carbon atom, with concomitant loss of HX to give the coordinatively stable metallocyclic complex. This mechanism, initially proposed by Parshall[36] and discussed extensively by Ryabov in his review entitled, "Mechanisms of Intramolecular Activation of C-H Bonds in

Transition-Metal Complexes",[9] has recently been supported by the isolation and characterisation of all intermediates in the cyclopalladation reaction of chiral phosphanes.[37]



Scheme 3

An alternative oxidative addition mechanism, the "nucleophilic pathway", gives a product in which the hydrogen from the carbon-hydrogen bond remains coordinated to the metal centre, the oxidation number of which increases by two units (scheme 4).[9] This hydrido complex may be isolated, or reductive elimination of HX may ensue (scheme 4) to give a final product which is indistinguishable from the complex which forms *via* the "electrophilic pathway" shown in scheme 3.[9]

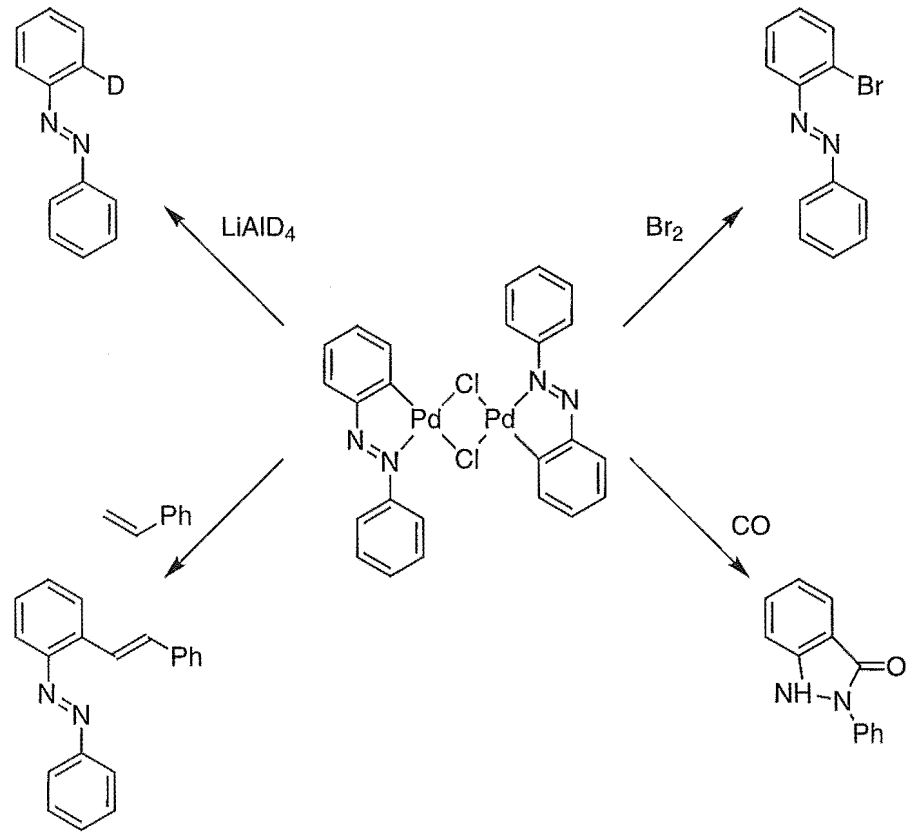


Scheme 4

Given that the product of the reaction is often the same, discriminating between the "oxidative addition/reductive elimination" and "electrophilic substitution" or a third multicentered pathway is rather complex.[9] Given that this research focuses on the preparation and characterisation of cyclometallated complexes, further discussion of these mechanistic conundra, beyond the assumption that the reactions described herein occur *via* an electrophilic mechanism, falls outside of the scope of this introduction.

The activation of a carbon-hydrogen bond, often in a site which is hindered to other reagents, has led to the widespread application of cyclopalladated complexes, in particular, as intermediates in organic synthesis. This topic has been the subject of two reviews,[5,16] and the applications include: selective deuterations (of the type discussed above for structural elucidation); selective halogenation; carbon-carbon bond formation *via* alkene insertion into the palladium-carbon bond; and the preparation of heterocycles

via insertion of carbon monoxide into the palladium-carbon bond (or by cyclisation of the products of the above-mentioned alkene insertions). Examples of these reactions, starting from the cyclopalladated azobenzene chloro-bridged dimer, are illustrated in scheme 5.[2]



Scheme 5

Related reactions, which have been the subject of much recent interest, are the insertion of alkynes into the carbon-palladium bond, together with investigation of the synthetic applications of the products of these reactions.[38] Coordination of chiral phosphines to optically active cyclopalladated benzylamines has been used both for chiral resolution as well as for NMR-based enantiomeric excess determinations.[39] Cyclometallated complexes can also be used as starting materials for other cyclometallated complexes prepared *via* transmetallation reactions (*vide infra*).

Cyclopalladation of 5-phenyl-1,4-benzodiazepin-2-one derivatives—for example, the tranquillisers Prazepam and Diazepam (Valium®)—has been used to selectively substitute the *ortho* position of the 5-phenyl group, such substitutions leading to improved activity of the drugs.[40] Cyclometallated complexes themselves

have been investigated for possible medicinal applications, particularly as potential chemotherapeutic anti-tumour agents. Recently, complexes of gold,[41] as well as those of palladium and platinum,[42] have been attracting the most attention.

Cyclometallated compounds, especially cyclopalladated complexes, have also found application in the burgeoning field of materials science where they are of use as: building blocks in self-assembly processes;[43] metalloreceptors;[44] and liquid crystals.[45]

In addition to the selective activation of a carbon-hydrogen bond, the effect that the formation of a metal-carbon bond has on the properties of the resultant complex, relative to complexes of *N,N*-bidentate analogues, has given rise to much interest in cyclometallated complexes. Investigations of cyclometallated complex photochemistry and luminescence have been used to probe their electronic properties and such studies of the complexes of iridium, osmium, palladium, platinum, rhodium and ruthenium have been reviewed.[46]

The replacement, in a complex, of *N,N*-bidentate ligands with cyclometallated analogues leads to higher energy ligand field (d-d) excited states. In addition, the strong σ-donor properties of these ligands enhances the ease of oxidation at the metal centre, thus promoting low energy metal-to-ligand charge-transfer excited states. This combination of effects leads to cyclometallated complexes which, relative to their *N*-donor analogues, have light absorption properties and low energy excited states well-suited to participation in photo-redox chemistry. Cyclometallated complexes have, therefore, potential applications as photosensitisers, possibly in solar energy conversion schemes.[47-50]

There are many nitrogen heterocycles which are able to form complexes in which two or more metal centres are bridged by a single ligand.[51] Studies of such complexes, and their cyclometallated analogues (*vide infra*), show that interactions between the coordinated metals are mediated by the π-system of the bridging ligand. These interactions, such as energy or electron transfer and magnetic coupling, may be influenced by altering the intermetal separation and the degree of conjugation between

the metal coordination sites within the ligand. Therefore, with the design of appropriate multiply cyclometallated ligands, there is the potential to 'tune' the magnitude of interaction between the metal centres. The resultant cyclometallated complexes, containing several metal atoms linked through a common bridging ligand, have potential applications in similar fields to their coordination complex analogues—the different electronic features of cyclometallated complexes offering the potential to prepare complexes with properties inaccessible through these coordination complexes. These applications include: multiple electron transfer catalysis; photosensitisation; and as components for molecular devices and low dimensional conducting polymers.[52]

This thesis, therefore, describes the synthesis and characterisation of a number of ligands, which are potentially capable of undergoing cyclometallation reactions, and their cyclo-rhodated and -palladated complexes, incorporating structural features described above. The ligands included in this study all incorporate nitrogen-containing heterocycles as the donor moiety and a number are potentially capable of giving doubly cyclometallated products.

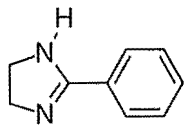
Chapter One

Ligands Containing Five-membered Heterocycles and One Cyclometallation Site

1.1 INTRODUCTION

This chapter describes the reactions of ligands in which the donor group is a nitrogen atom within a five-membered heterocycle. The ligands discussed include those with two heteroatoms, their benzo-fused analogues and one with three heteroatoms. Whilst the cyclopalladation of a number of the ligands discussed in this chapter have been previously reported, the cyclorhodations herein described, and the subsequent ligand exchange reactions, all yield previously unknown complexes. The previously unexplored coordination chemistry and attempted cyclometallations of three phenyloxazoles are reported, as is the preparation of a complex in which the oxazole is mercurated.

1.2 FIVE-MEMBERED HETEROCYCLES WITH TWO HETEROATOMS



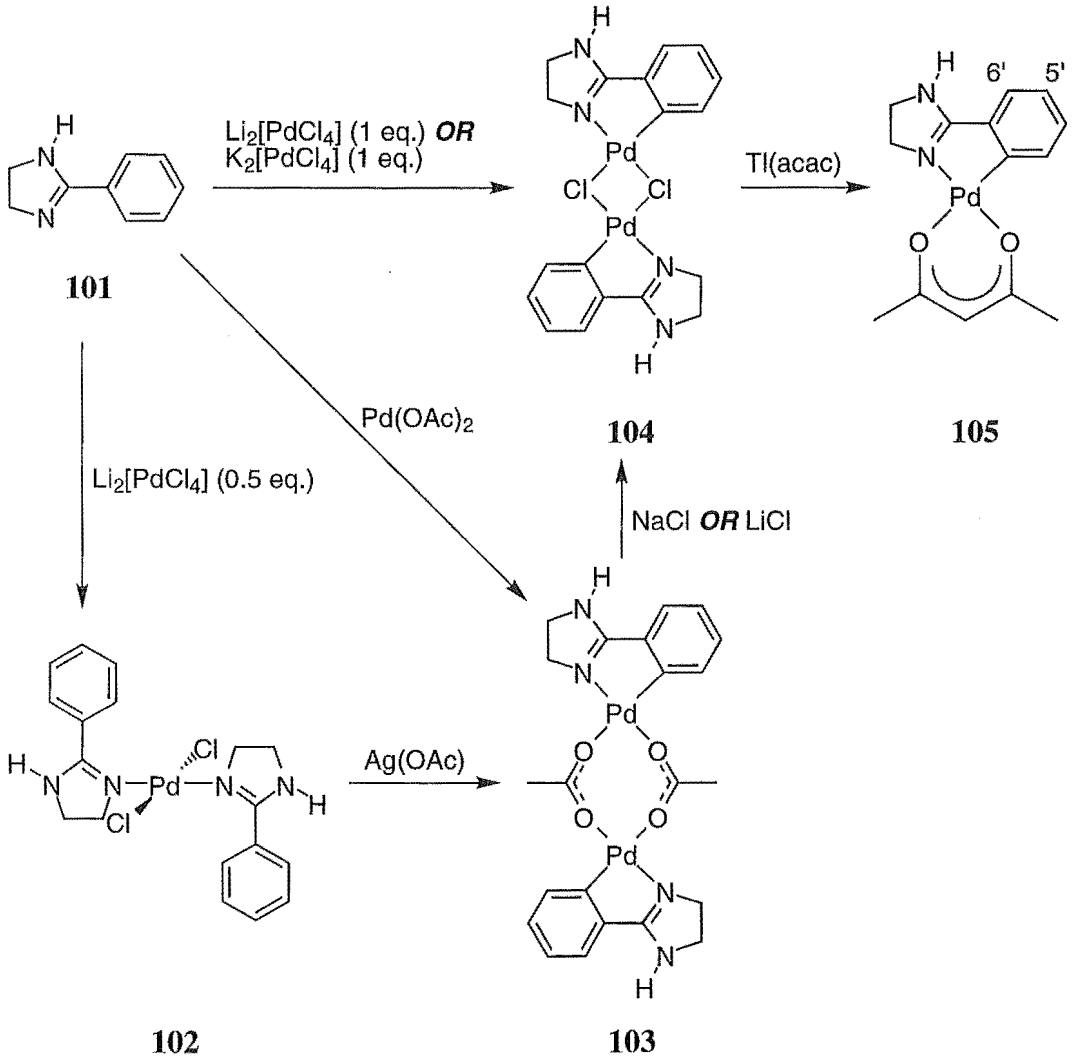
101

Initial investigation of the cyclometallation of the commercially available ligand 2-phenylimidazoline (**101**) was concerned with its possible cyclorhodation. Reaction of this ligand with rhodium trichloride trihydrate in 2-methoxyethanol was unsuccessful, giving an insoluble black precipitate, so the reaction was repeated with ethanol as solvent. This gave a heterogeneous mixture of yellow, brown and black solids. Reaction of this product with sodium acetylacetonate gave an off-white solid, which was insoluble in common NMR solvents and remains uncharacterised.

In 1996 a paper detailing the coordination chemistry of **101** with palladium(II) and platinum(II)—including its cyclo-palladation and -platination—was published.[53] The only mononuclear complex described was the coordination complex **102**, whilst the cyclopalladated complexes described, the acetate-bridged complex **103** and the chloro-bridged complex **104**, are dimeric. Both of these cyclopalladated complexes

were prepared by direct reaction of the ligand with the appropriate palladium(II) salt or by reaction of **102** with silver acetate to give **103** which was then converted to **104** by acetate-chloride metathesis (scheme 1.1).

The reaction of palladium acetate and the ligand in acetic acid and subsequent conversion of the resultant acetate-bridged dimer, **103**, to the corresponding chloro-bridged complex, was reported to give **104** in 24% yield (based on palladium).[53] The reaction of palladium acetate and **101** was repeated in benzene as these conditions have been found, during the course of this work, to give cyclopalladated complexes of several ligands which could not be obtained by such reaction in acetic acid (*vide infra*).



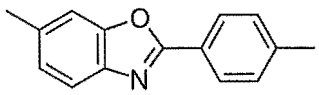
Scheme 1.1

This reaction, followed by acetate-chloride metathesis with lithium chloride, gave **104** in comparable (28%) yield. The resonances in the ^{1}H NMR spectrum of **103**—a sample

of which was isolated as an intermediate in this preparation—had chemical shifts in agreement with those reported.[53] The chloro-bridged dimer, **104**, was not characterised but was subjected to ligand exchange with thallium acetylacetonate to give the desired, mononuclear complex, **105** (scheme 1.1) in 8% overall yield (based on palladium).

The previously unreported acetylacetonate complex, **105**, was completely characterised by microanalysis and ^{1}H and ^{13}C NMR spectroscopy. The resonances for H-5' and H-6' overlap and their chemical shifts could not, therefore, be separated. The chemical shifts for C-5' (123.58 ppm) and C-6' (123.25 ppm) were assigned on the basis of the observation that, in the spectra of all the reported complexes of **101**, the chemical shift for C-5' is always slightly upfield relative to that for C-6'.[53]

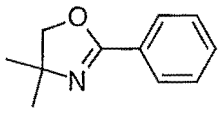
The cyclopalladation—and subsequent conversion of the chloro-bridged dimer to the mononuclear acetylacetonate complex—of 2-phenylbenzoxazole has been previously reported.[54] This extended the work on the cyclopalladations of such ligands, the first such report—concerning the reactions of 2-*p*-tolylbenzoxazole and its 6-methylated analogue (**106**) with palladium acetate—having been published in 1980.[55] Moreover, the synthesis and NMR structural analysis of several cyclopalladated complexes of 2-phenylbenzoxazole have recently been published,[56] demonstrating the continuing interest in the cyclopalladated complexes of such ligands.



106

In addition to the published work on phenylbenzoxazoles discussed above, the cyclometallation chemistry of alkyl- and aryl-2-oxazolines has also been the subject of continuing attention in the literature. Reaction of 2-t-butyl-4,4-dimethyl-2-oxazoline with palladium acetate gives dimeric and trinuclear complexes in which the oxazoline nitrogen directs palladation of one of the methyl groups of the t-butyl substituent.[57] Similarly, 4,4-dimethyl-2-phenyloxazoline (**107**) and a number of its phenyl-substituted derivatives have been cyclopalladated by direct reaction with palladium acetate.[58] The acetate bridged dimers formed in these reactions have been reacted with carbon

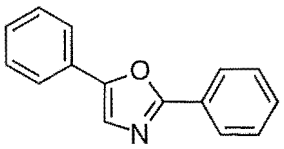
monoxide to give diarylketones[58] and with alkyl halides to give regioselectively *ortho*-alkylated derivatives.[59]



107

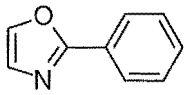
Related 4,4-dimethyl-2-phenyloxazolines have also been *ortho*-lithiated—the lithiation being directed by the oxazoline heteroatoms—and these species transmetallated to give the *ortho*-cuprated complexes[60] which, in turn, can be used to prepare the *ortho*-stannylated analogues.[61] Such *ortho*-stannylated and *ortho*-mercurated derivatives can also be prepared by transmetallation of the *ortho*-lithiated species or, in the case of the latter, by direct reaction of the ligand with mercury(II) acetate.[62] Transmetallation of the *ortho*-mercurated 4,4-dimethyl-2-phenyloxazolines so prepared, with tetramethylammonium tetrachloroaurate(III), has been shown to give cycloaurated analogues of the cyclopalladated complexes discussed above.[30a]

Given the considerable interest in the cyclometallation chemistry of both phenylbenzoxazoles and phenyloxazolines, it is surprising that there are not more investigations of the coordination chemistry of phenyloxazoles reported in the literature. A literature search revealed that 2,5-diphenyloxazole (**108**) is the only ligand of this type for which there have been any such reports. In 1973, Cockburn *et al.* reported that the treatment of **108** with sodium tetrachloropalladate gives the mononuclear coordination complex, *trans*-Pd(**108**)$_2$Cl$_2$.[63] A subsequent account of the reactions of **108** with palladium(II) and platinum(II) came to the conclusion that the ligand, "behaves generally as monodentate N-bonded with the exception of MLX_2" and, furthermore, "In these MLX_2 complexes the 2,5-diphenyloxazole acts as a bridging ligand".[64] The authors noted that this coordination behaviour is similar to that found for 3,5-diphenylisoxazole, the structural analogue of **108**.[65] The only reported cyclometallated complex containing an oxazole ring as the non-carbon donor is obtained upon the reaction of **108** with pentacarbonylmethylmanganese.[66]



108

Consideration of phenyloxazoles, other than **108**, which have the nitrogen donor atom in the necessary position to direct metallation of the phenyl ring gives 2-phenyloxazole (**109**) and 4-phenyloxazole (**110**) as ligands which might be cyclometallated. The ligand 2,4-diphenyloxazole (**111**), would offer the opportunity to further investigate the subtleties of regioselection in the cyclometallation reaction. The two stereochemically and electronically inequivalent phenyl rings in this ligand are both suitably positioned for cyclometallation with respect to the nitrogen atom and the preferential cyclometallation of one of these would give useful information in this respect.



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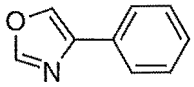

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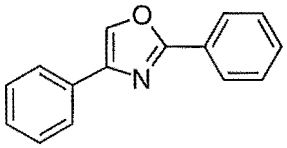


111

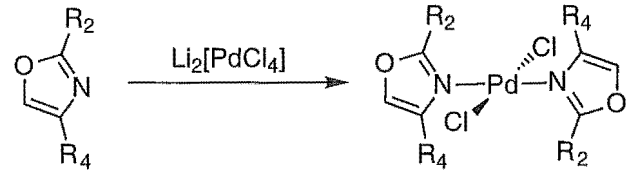
A search of the literature showed that the three oxazoles above are well-known, with relatively straightforward preparations. The serendipitous preparation of 2-(*ortho*-nitrophenyl)-oxazole, its hydrogenation and subsequent deamination—*via* the diazonium derivative—gave **109** in reasonable yield, this being the first reported synthesis of this oxazole.[67] Seeking a more convenient synthesis led to a paper in which the preparation of **109** by the condensation of vinylene carbonate and benzamide is described.[68] This reaction was repeated, the crude oxazole obtained from the reaction mixture being characterised by ^{1}H and ^{13}C NMR spectroscopy[69-72] and used without further purification.

The isomeric phenyloxazole, **110**, was prepared from 2-bromoacetophenone and ammonium formate according to the literature procedure.[73] The oxazole was purified

by distillation under reduced pressure and characterised by ^{1}H and ^{13}C NMR spectroscopy.[69,74]

The first reported synthesis of **111**, from 2-bromoacetophenone and benzamide, was in 1884 and this remains the most convenient preparation of this compound.[75] Rather than distill the crude compound, as in the above mentioned report, it was found that purification was more conveniently achieved by recrystallisation from ethanol[70] and the resultant white crystalline solid was fully characterised.

Investigation of the coordination chemistry of these three oxazoles began with their reactions with lithium tetrachloropalladate. For **109** and **110** the reactions gave the yellow coordination complexes, Pd(**109**)$_2$Cl$_2$ and Pd(**110**)$_2$Cl$_2$ (**112** and **113**, respectively) (scheme 1.2). These complexes are analogues of *trans*-Pd(**108**)$_2$Cl$_2$, which is the product of a similar reaction with the diphenyloxazole **108** (*vide supra*). The complexes are assigned the *trans* stereochemistry on the basis of the reported stereochemistry of this analogous complex and the observation that, in the ^{1}H and ^{13}C NMR spectra of each complex, the two ligands are equivalent. It is interesting to note that whilst **109** is quite soluble in chloroform, **110** is only sparingly soluble in this solvent but dissolves readily in DMSO.



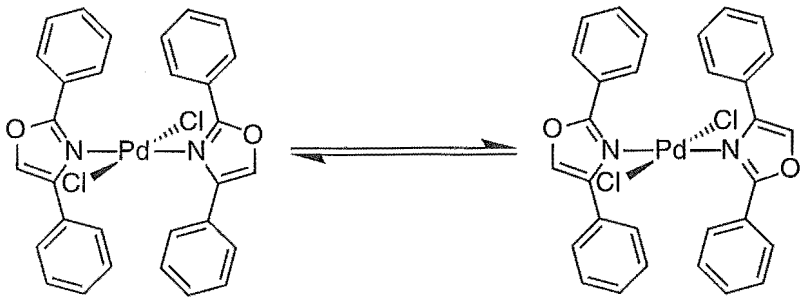
109 R_2=Ph, R_4=H
110 R_2=H, R_4=Ph

112 R_2=Ph, R_4=H
113 R_2=H, R_4=Ph

Scheme 1.2

Reaction of **111** with lithium tetrachloropalladate gave a yellow solid which is sparingly soluble in chloroform. Examination of the FAB mass spectrum shows a peak corresponding to Pd(**111**)$_2$Cl$^+$, presumably formed *via* loss of a chloride ion from the coordination complex, Pd(**111**)$_2$Cl$_2$. Acquisition of a ^{1}H NMR spectrum in $CDCl_3$ showed that the product appears to be a mixture of two complexes in an approximate

one:two ratio, the relative composition of which remains unchanged after several days in solution. The spectrum clearly shows two pairs of doublets* which can be assigned to the resonances due to the *ortho* protons, indicating that each of the ligands in the two complexes is unmetallated. The appearance of the spectrum changes very little with increasing temperature, suggesting that any dynamic process leading to interchange between the complexes is slow on the NMR time-scale, and that the temperature limit of the spectrometer is somewhat below the coalescence temperature. The two complexes are thought to be *syn* and *anti* rotamers which are in equilibrium, but interconvert relatively slowly, due to the steric interaction between ligands upon rotation about the palladium-nitrogen bond (scheme 1.3). This contrasts with the observed temperature dependence of the NMR spectra of related palladium coordination complexes for which the *syn* and *anti* rotamers interconvert more rapidly (*vide infra*).



SYN *ANTI*

Scheme 1.3

Having established that reaction with lithium tetrachloropalladate does not lead to cyclopalladation of the three phenyloxazoles, their reactions with palladium acetate were investigated. These reactions were performed in a variety of solvents, both at room temperature and under reflux, and were not successful. Similarly, reaction with rhodium trichloride failed to give cyclorhodated complexes. In the reactions of **110** and **111**, apparent reduction of the rhodium(III) to rhodium metal—indicated by the formation of a tenacious, silvery mirror on the inside of the reaction flask—was observed.

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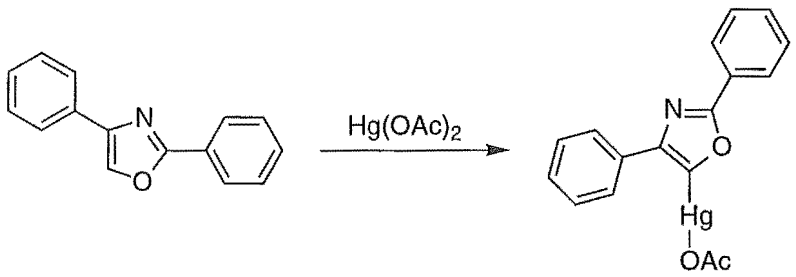
* Throughout this thesis, resonances in ^{1}H NMR spectra are described according to their first order couplings only. The 1D-TOCSY experiment, which permits the isolation of individual spin systems within a given molecule has rendered the consideration of longer range couplings largely unnecessary.

In 1982, Wardell wrote; "Transfer of organic groups from mercury to other metals is a well established and indeed a classic synthetic route to organometallics."[76] This same route, namely the formation of organomercurials and their subsequent reaction (transmetallation) with labile transition metal compounds, has been used to prepare, for example: cyclo-aurated;[30a,77,78] -palladated;[79-81] -rhodated;[82,83] and -ruthenated[80] complexes, some of which are otherwise inaccessible. This method seemed to offer an attractive route to the preparation of cyclometallated phenyloxazoles, given that it had been established that such complexes could not be prepared directly.

Attempted mercuration of **109** or **110** with mercuric acetate in refluxing ethanol[84] was unsuccessful. Instead, apparent reduction of the mercury(II) to elemental mercury, with the formation of a small amount of motile, grey liquid phase, was observed—the small quantity of precipitate formed being insoluble in common NMR solvents.



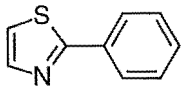
111 **114**

Scheme 1.4

In contrast, reaction of **111** under the same conditions gave a pale yellow precipitate which is soluble in both chloroform and DMSO. The ^{1}H and ^{13}C NMR spectra of this solid have resonances characteristic of the acetate ligand and its presence was confirmed with the recording of an IR spectrum. The NMR spectra, however, show signals which can be assigned to resonances from two inequivalent, monosubstituted phenyl rings and this clearly demonstrates that the complex was not cyclometallated. The ^{1}H NMR spectrum of the free ligand exhibits a singlet resonance assigned to the signal from the sole proton, attached to C-5, on the oxazole ring, whilst the spectrum of the complex has no such resonance. Microanalysis of the solid returned the stoichiometry Hg(**111**-H)(OAc), and the structure of this complex is, therefore,

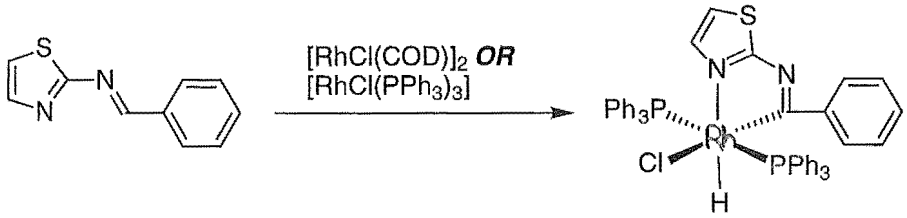
assumed to be **114**, which forms *via* an oxygen-directed mercuration of the oxazole ring at C-5 (scheme 1.4).

The cyclopalladation of 2-phenylthiazole (**115**), the sulfur analogue of **109**, with palladium acetate has previously been reported.[85] This paper also reported the conversion of the resultant acetate-bridged dimer into a number of mononuclear derivatives, including the palladium acetylacetonate complex which has subsequently been fully characterised by ^{1}H and ^{13}C NMR.[54]



115

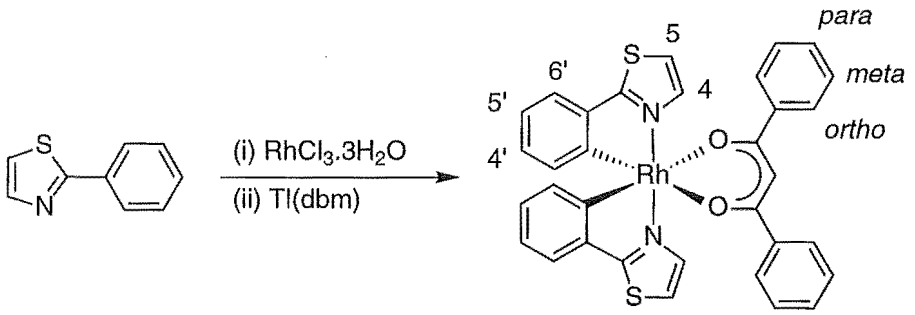
Whilst there are no literature reports of **115** having been cyclorhodated, the thiazole ring has been used to provide the nitrogen donor atom in a number of analogous complexes in which an imine—as opposed to an arene —carbon-hydrogen bond has been activated. Reaction, in THF, of suitable rhodium(I) reagents with 2-benzylideneaminothiazole and excess triphenylphosphine gives the cyclometallated rhodium(III) complex in which the imine C-H has undergone oxidative addition to the metal (scheme 1.5).[86] Repeating this reaction with a variety of phenyl-substituted analogues of this ligand gave a number of related cyclorhodated complexes.



Scheme 1.5

Reaction of **115** with rhodium trichloride gave a chloro-bridged dimer, which was characterised by ^{1}H NMR spectroscopy and microanalysis, the latter because the dimer was recrystallised prior to its use in ligand exchange reactions. Attempted ligand exchange reactions with sodium ß-diketonates in methanol failed to give the desired mononuclear complexes in sufficient yield to permit their complete characterisation, the reaction with sodium benzoylacetonate not yielding any product at all. The ligand

exchange reactions were repeated using thallium acetylacetonate and thallium dibenzoylmethanate to give the desired mononuclear complexes, Rh(**115**-H)$_2$(acac) and Rh(**115**-H)$_2$(dbm) (**115a**)(scheme 1.6), as crystalline solids in adequate yield. These complexes were fully characterised by ^{1}H and ^{13}C NMR spectroscopy and microanalysis.



115 **115a**

Scheme 1.6

Whilst the ^{1}H NMR spectra of these two complexes are relatively straightforward, their assignment provides a typical illustration of the use of homonuclear irradiation (selective proton decoupling) experiments. For example, the ^{1}H NMR spectrum of **115a**(figure 1.1a) has all the signals of interest within the range of chemical shifts; $6.2 < \delta < 8.0$ ppm. In the assignment of this spectrum, the only difficulty is in the assignment of the resonances corresponding to the cyclometallated phenyl ring. Specifically, whilst on the basis of chemical shift the doublet at 6.41 ppm can be assigned as being from H-3' on this ring and the doublet at 7.52 ppm as being from H-6', assignment of the triplets at 6.85 ppm and 6.92 ppm—which correspond to H-4' and H-5'—is not possible from this spectrum alone. Figure 1.1b shows the spectrum resulting from homonuclear decoupling of the doublet at 6.41 ppm (H-3'). The triplet at 6.85 ppm collapses to a doublet whilst the long range coupling is lost from the triplet at 6.92 ppm, thereby identifying these signals as being due to a proton *ortho* and *meta* to that being irradiated; that is H-4' and H-5' respectively, and thus completing the assignment of the ^{1}H NMR spectrum.

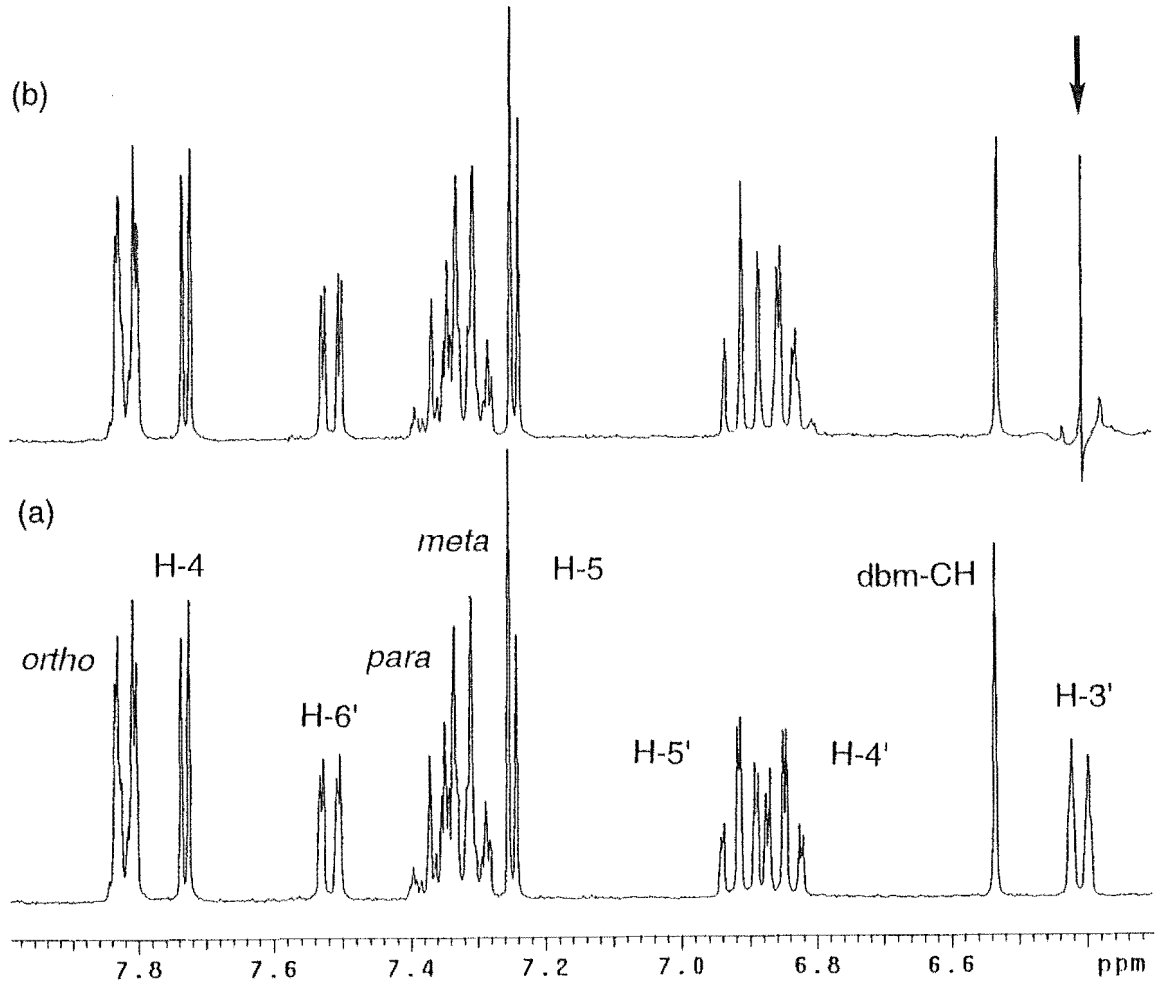
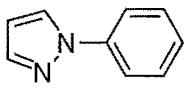


Figure 1.1 (a) ^{1}H NMR spectrum ($CDCl_3$) of **115**q

(b) Decoupled (6.41 ppm) ^{1}H NMR spectrum ($CDCl_3$)of **115**q

1.3 BENZO-FUSED FIVE-MEMBERED HETEROCYCLES WITH TWO HETEROATOMS



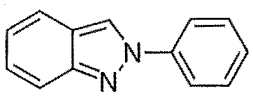
116

The metallation chemistry of 1-phenylpyrazole (**116**) has been extensively investigated.[4,36,54,66,85,87-99] The first account of the metallation of **116** was in 1958 when the reaction of the ligand with n-butyllithium was reported.[87] The cyclopalladation of **116** was cited as a private communication in 1970,[36] the reactions with palladium(II) being fully reported three years later.[4] Ever since these first reports,

there has been on-going interest in the cyclometallated complexes of **116** and the ligand has—in addition to palladium[54,88,89]—been directed cyclometallated with: chromium;[90] cobalt;[90] iridium;[91] manganese;[66] mercury;[85] platinum;[88] rhodium;[92-94] and ruthenium.[95]

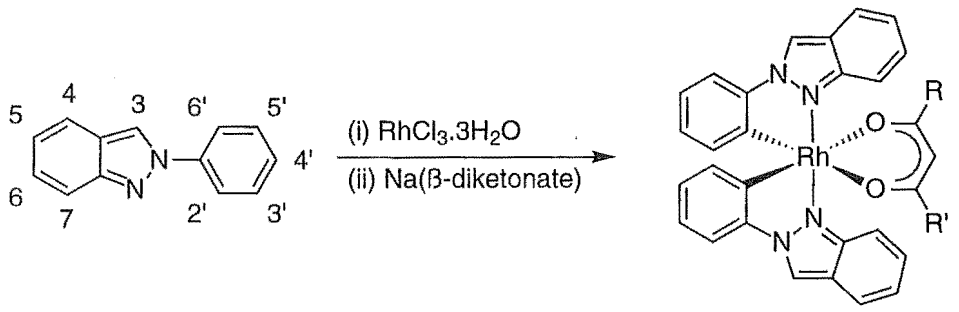
Reaction of **116** with rhodium trichloride trihydrate gives a chloro-bridged, cyclorhodated dimer.[91] This complex has been crystallographically characterised[94] and converted into corresponding mononuclear rhodium ß-diketonate complexes.[96] In addition, the *ortho*-lithiated species has been used to prepare the bis-ligand, homoleptic cyclometallated complex with platinum.[97,98] Also, analogous tris-ligand homoleptic complexes have been prepared from reaction of the corresponding Grignard reagent with cobalt, chromium, nickel, titanium or vanadium precursors.[99]

In contrast to the many reports of the cyclometallation chemistry of **116**, there is only one paper in the literature which reports the cyclometallation of its benzo-fused analogue, 2-phenylindazole (**117**), with palladium.[89] Given the ease with which **116** is cyclorhodated, it was thought that the reaction of **117** with rhodium trichloride warranted investigation.



117

Reaction of **117** with rhodium trichloride trihydrate gives a cyclorhodated, chloro-bridged dimer, [Rh(**117**-H)$_2$Cl]$_2$, in good yield. This pale yellow solid was characterised by ^{1}H NMR spectroscopy. The ligand exchange reactions of this complex with sodium ß-diketonates were straightforward and gave the corresponding mononuclear rhodium ß-diketonate complexes—Rh(**117**-H)$_2$(acac) (**118**); Rh(**117**-H)$_2$(dbm) (**119**); and Rh(**117**-H)$_2$(bac) (**120**)—in good to excellent yields (scheme 1.7). All of these rhodium ß-diketonate complexes were fully characterised by ^{1}H and ^{13}C NMR spectroscopy and, following recrystallisation, by microanalysis.



117

118 R=R'=CH_3
119 R=R'=C_6H_5
120 R=CH_3, R'=C_6H_5

Scheme 1.7

The assignment of the ^1H NMR spectrum of the acetylacetonate complex, **118**, is complicated by the overlap of the resonances for H-6 and H-6' and those for H-4 and H-7. The signals in the corresponding ^{13}C NMR spectrum, however, are well-separated and the acquisition of a heteronuclear multiple quantum coherence (HMQC) spectrum, combined with the use of selective proton decoupling experiments, enabled the full assignment of all signals in the NMR spectra.

The resonances due to the cyclorhodated 2-phenylindazole ligands in the ^1H NMR spectrum of the corresponding dibenzoylmethanate complex, **119** (figure 1.2), have chemical shifts similar to those in the spectrum of **118**. Assignment of these, however, is hampered by the positions of the resonances due to the aromatic protons of the dibenzoylmethanate ligand. All three of these resonances, together with seven of the nine due to the cyclorhodated 2-phenylindazole ligands, have chemical shifts within the range $6.6 < \delta < 7.8$ ppm. Despite the proximity of the signals, a tentative assignment based on chemical shift and spin-spin coupling information is possible. The ^{13}C NMR spectrum of this complex has all twelve aromatic protonated carbons separated by at least 0.3 ppm, their chemical shifts within the range $112 < \delta < 136$ ppm. Again, tentative assignment of many of these signals is possible, based on the information provided by their chemical shifts. The HMQC spectrum (figure 1.3) of the aromatic regions clearly shows all expected correlations and can be used to confirm unambiguously the tentative assignments of both the ^1H and ^{13}C NMR spectra.

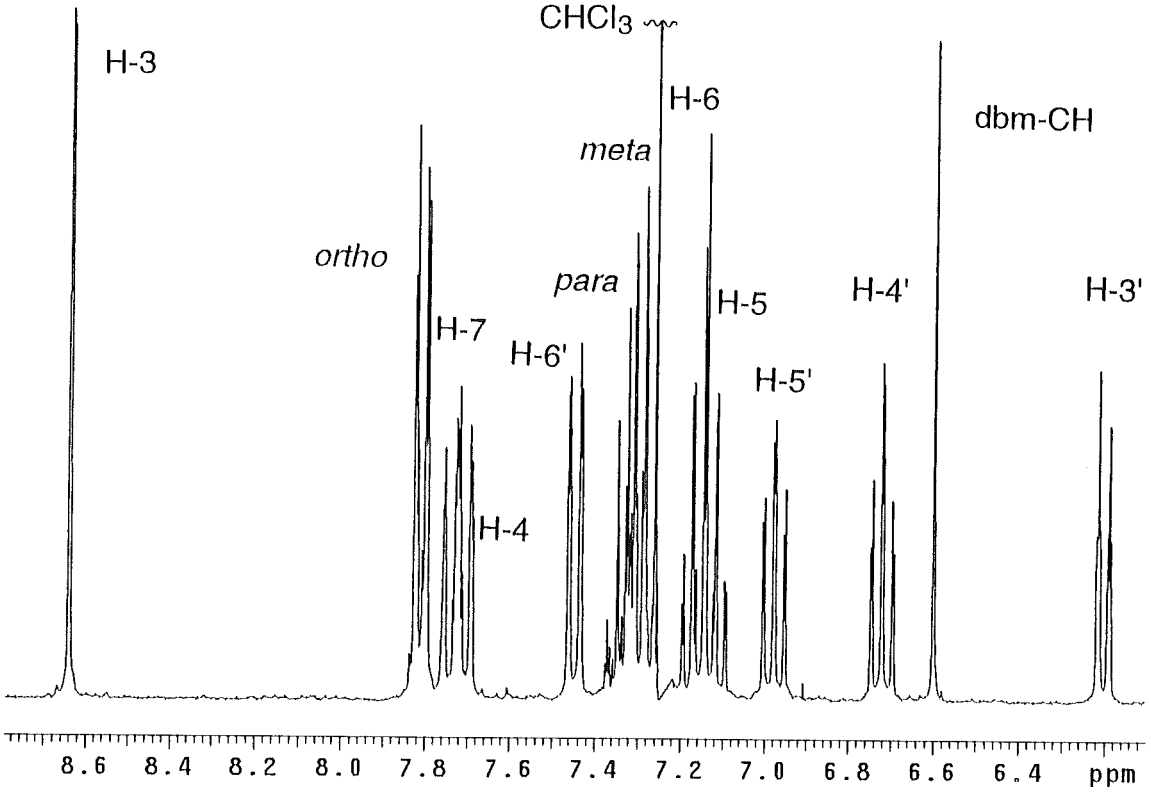


Figure 1.2 ^{1}H NMR spectrum of **119**

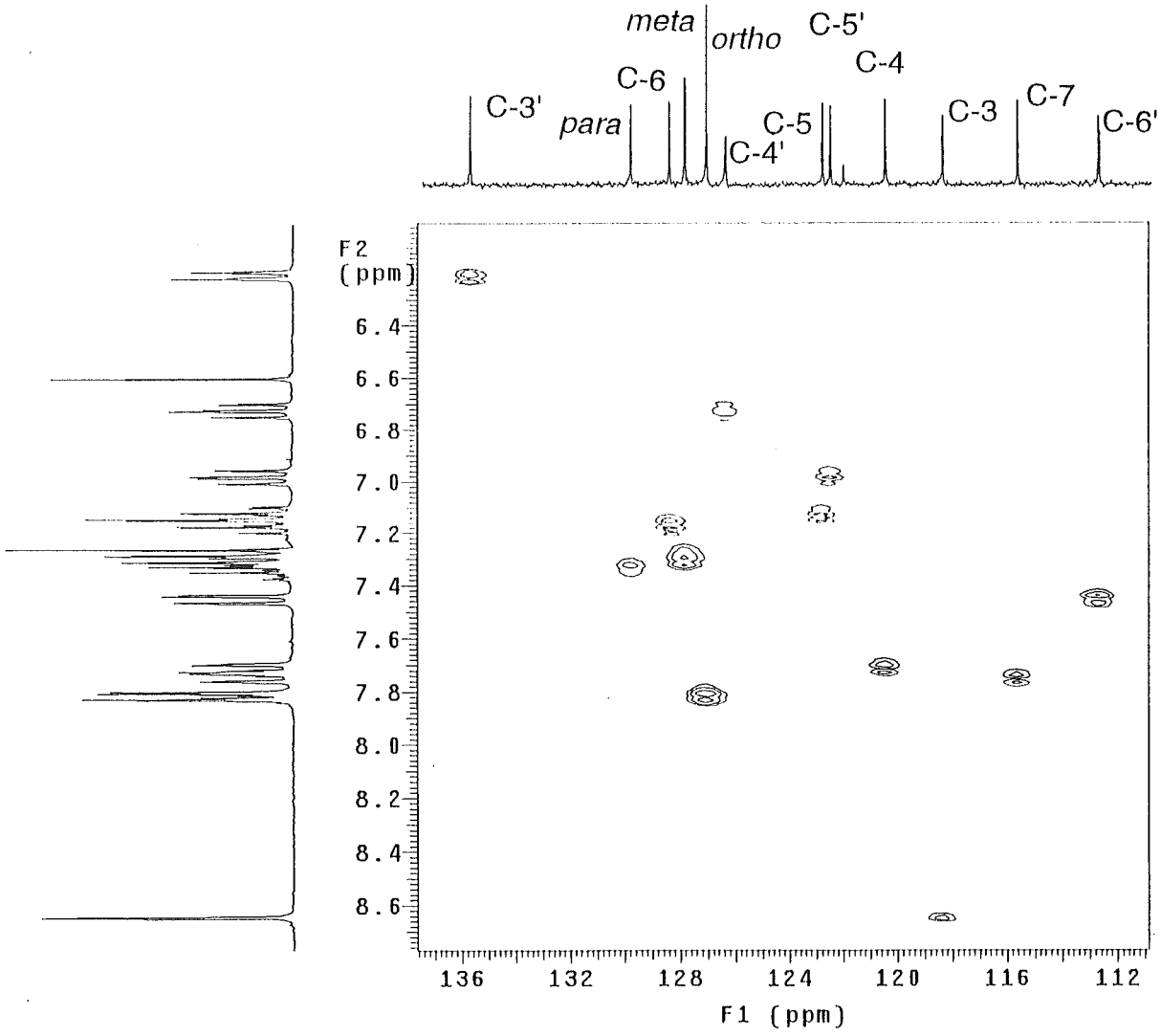


Figure 1.3 HMQC spectrum of **119** showing the twelve expected correlations.

Reaction of **116** with rhodium trichloride trihydrate gives a chloro-bridged, cyclorhodated dimer, [Rh(**116**-H)$_2$Cl]$_2$.[92,94] Of the two likely isomers that might be formed in the reaction—the *racemic* diastereoisomer (D_2 symmetry) or the *meso* diastereoisomer (C_{2h} symmetry)—the structure of the complex was crystallographically determined to be the *racemic* isomer.[94] The formation of this isomer was attributed to steric factors, as molecular models indicated that the *meso* diastereoisomer would have strong steric interactions between the protons on C-3 of the mirror related pyrazoles.[94] Attachment of a benzo moiety to the pyrazole rings of [Rh(**116**-H)$_2$Cl]$_2$ to form the indazole rings of [Rh(**117**-H)$_2$Cl]$_2$ would considerably increase the steric interactions between the mirror related N-donor rings, thereby further disfavouring formation of the *meso* diastereoisomer. Hence it is assumed that, in the case of **117** and, indeed, all other ligands in this work, steric reasons dictate that the chloro-bridged rhodium dimer obtained upon reaction with rhodium trichloride trihydrate has the structure of the *racemic* diastereoisomer.

Preparation of **118** and **119**, by ligand exchange from [Rh(**117**-H)$_2$Cl]$_2$ with the symmetrical acetylacetonate or dibenzoylmethanate anions, gives mononuclear complexes with C_2 symmetry. Both cyclorhodated ligands within such complexes are equivalent, and this is reflected in their NMR spectra. However, upon exchange with the unsymmetrical benzoylacetonate anion, the resultant mononuclear complex, **120**, has a structure which has no symmetry elements. Therefore, the two cyclorhodated ligands within this complex are inequivalent, one being coordinated *trans* to the phenyl ring of the chelated benzoylacetonate ligand, the other *trans* to the methyl group.

In principle, each of the atoms in analogous positions in the two different cyclorhodated ligands of **120**, and, indeed, any such rhodium benzoylacetonate complex, should have different chemical shifts in the ^{1}H and ^{13}C NMR spectra. In practice, however, the difference in the magnetic environments of such atoms may be relatively minor and their observed chemical shifts accidentally equivalent. Hence, not all signals in the ^{1}H and ^{13}C NMR spectra of **120** (figures 1.4 and 1.5 respectively) are resonances for individual atoms with different chemical shifts,

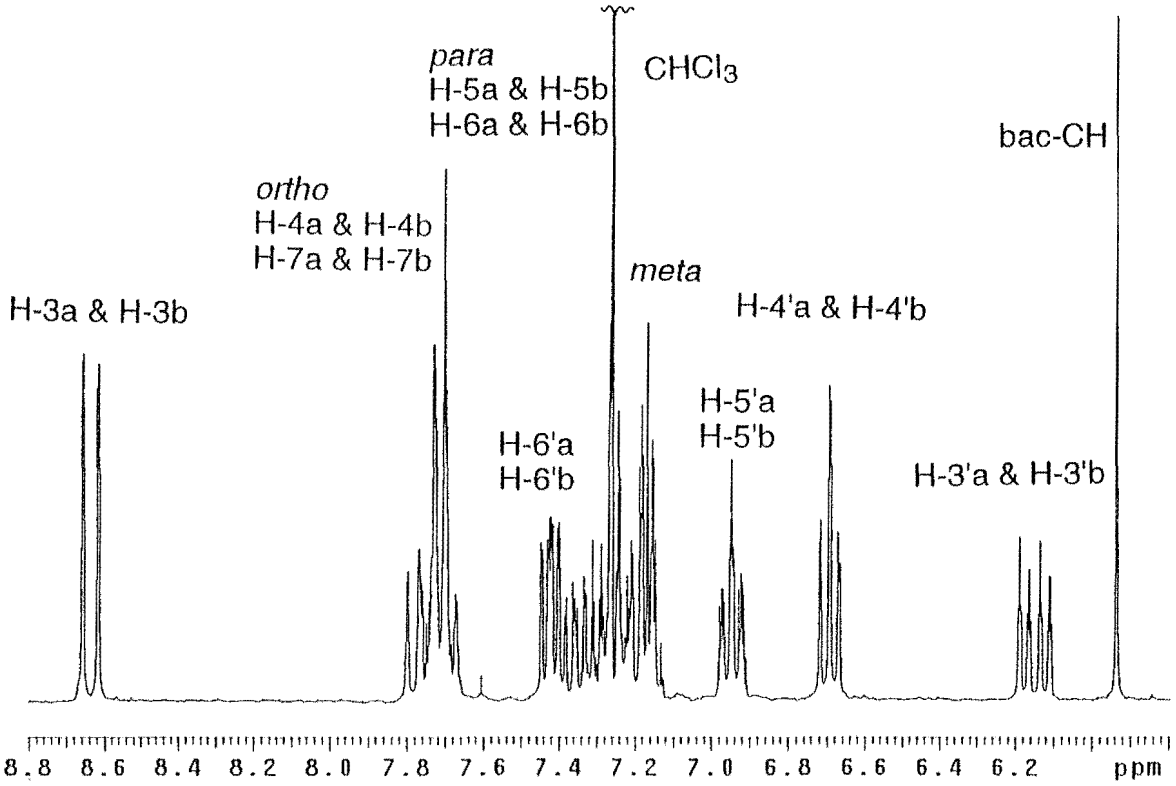


Figure 1.4 Partial ^{1}H NMR spectrum of **120**; *c.f.* figure 1.2

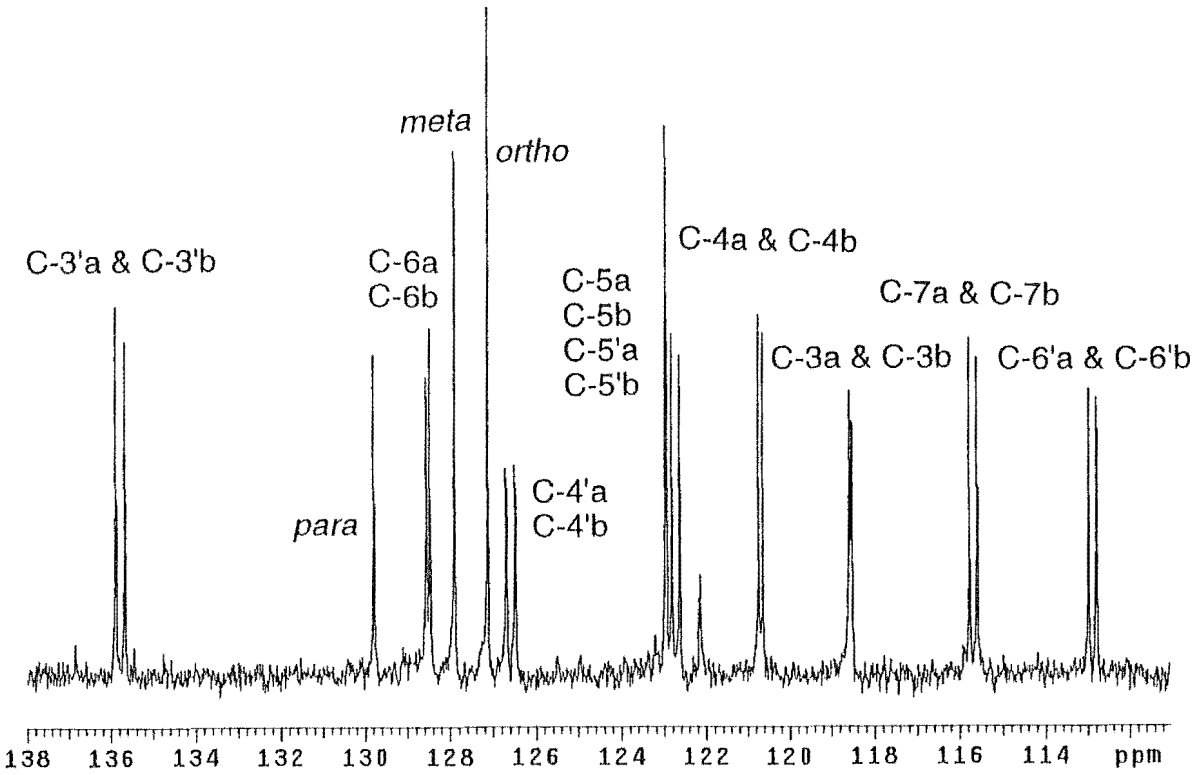
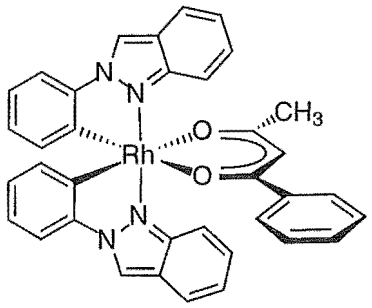


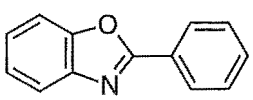
Figure 1.5 Partial ^{13}C NMR spectrum of **120**

some arise from the resonances of several atoms and individual chemical shifts cannot, therefore, be assigned. This often means that within such a complex, a given signal can only be assigned to a specific position in one or other of the two ligands but not to a specific ligand. When reporting the spectra of these complexes, for the purposes of distinguishing between the resonances arising from atoms in analogous positions in each of the two different cyclorhodated ligands, the assignments are arbitrarily assigned the subscripts "a" and "b". For example, H-3'a and H-3'b refer to protons in the same position—adjacent to the rhodium-carbon bonds—on each of the two cyclorhodated ligands. It is important to understand that these subscripts, being arbitrarily assigned, have no geometrical basis and are merely a convenient method for reporting the spectra, whilst indicating the presence of signals arising from analogous positions in two inequivalent cyclorhodated ligands within the same complex .



120

Whilst the phenyloxazoles **109**, **110** and **111** could not be cyclometallated, the cyclopalladation of the benzo-fused analogue, 2-phenylbenzoxazole (**121**), has been previously reported.[54,56] Reaction of this ligand with rhodium trichloride trihydrate in refluxing 2-methoxyethanol gives, in 72% yield, a chloro-bridged dimer, $[Rh(\mathbf{121}\text{-}H)_2Cl]_2$ (**122**), as a light brown solid, which was characterised by ^1H NMR spectroscopy (scheme 1.8).



121

The ^{1}H NMR spectrum of **122** (figure 1.6) unequivocally confirms the cyclorhodated structure of the complex. The spectrum has all eight expected resonances—four each due to the cyclometallated phenyl ring and the benzoxazole moiety of the ligand—within the aromatic region. The doublets at 6.22 ppm and 8.24 ppm are assigned to the signals due to H-3' and H-4 respectively, on the basis of chemical shift. H-3' has a coordination induced shift (CIS) of -1.33 ppm relative to the free ligand, due to the shielding ring current of the cyclometallated ring of the other ligand. H-4, however, has a CIS of 0.45 ppm as it lies above a chlorine atom and is consequently deshielded relative to its environment in the free ligand. Given this, assignment of the remaining resonances, using selective proton decoupling or 2D-correlation spectroscopy (COSY) experiments, is straightforward.

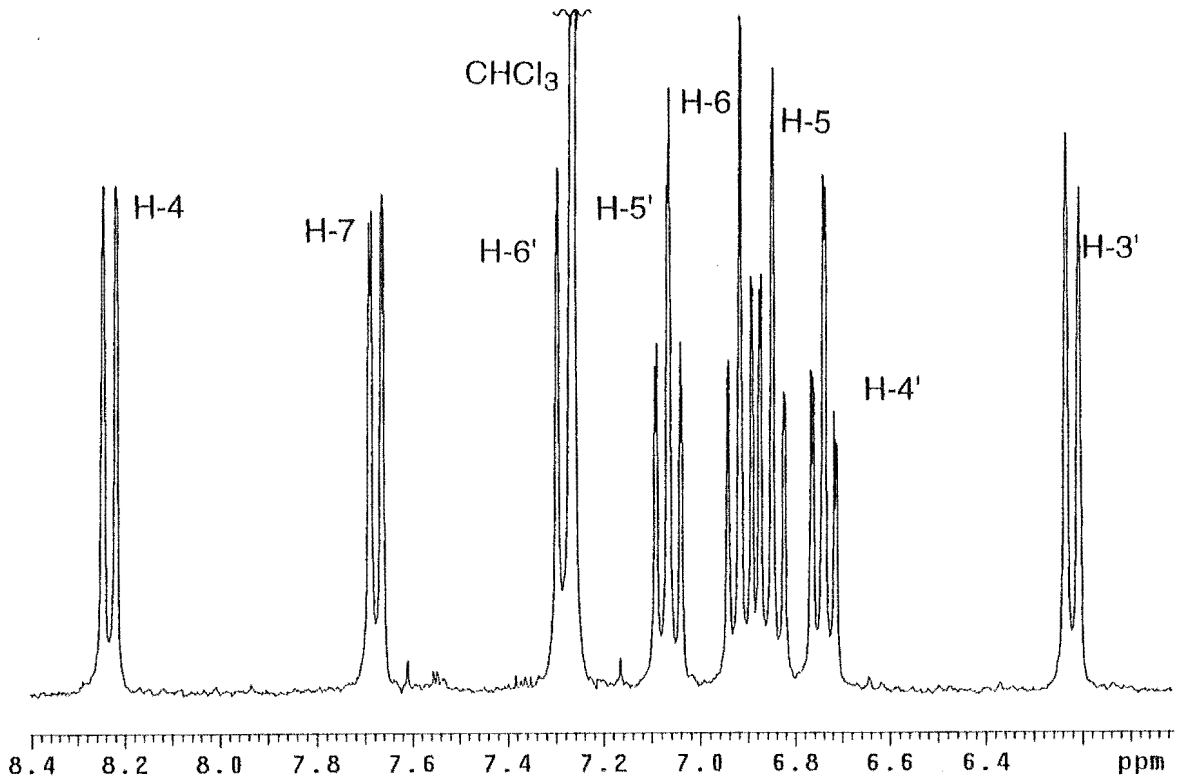
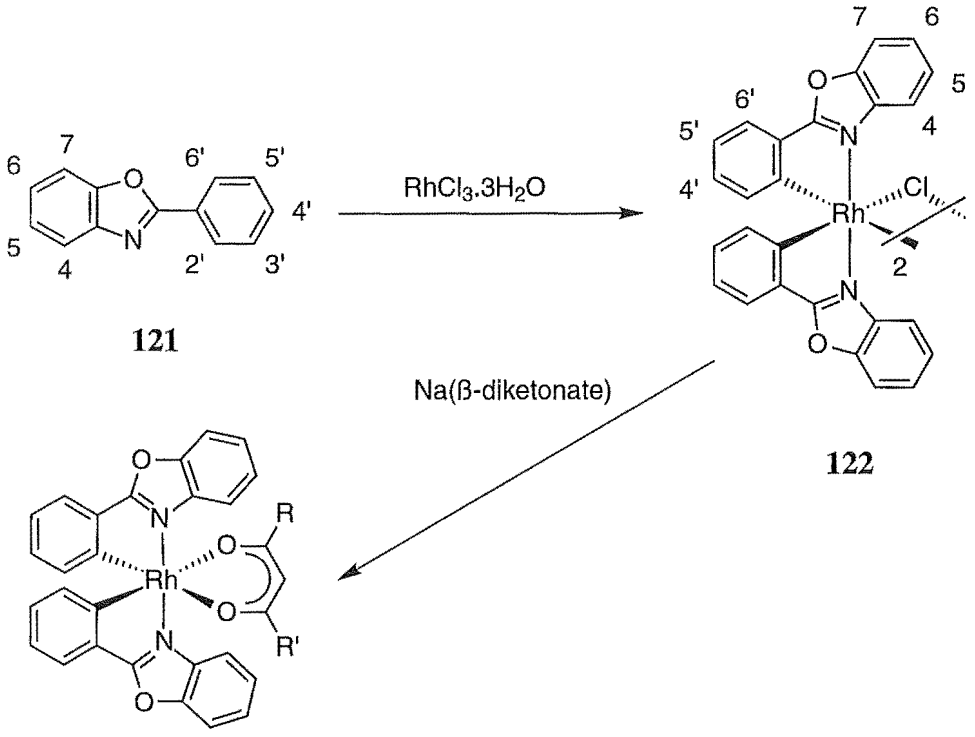


Figure 1.6 ^{1}H NMR spectrum of **122**

Ligand exchange reactions of this complex with the appropriate sodium ß-diketonate gave the corresponding mononuclear complexes—Rh(**121**-H)$_2$(acac) (**123**); Rh(**121**-H)$_2$(dbm) (**124**); and Rh(**121**-H)$_2$(bac) (**125**)—as yellow powders in excellent yield (scheme 1.8). The crude powders showed some contamination by the

chloro-bridged dimer, **122**; however, after recrystallisation, these three rhodium ß-diketonate complexes were fully characterised by microanalysis and ^{1}H and ^{13}C NMR spectroscopy.



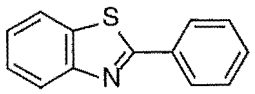
121

122

123 R=R'=CH_3
124 R=R'=C_6H_5
125 R=CH_3, R'=C_6H_5

Scheme 1.8

The cyclopalladation of 2-phenylbenzothiazole (**126**), the sulfur analogue of **121**, has previously been reported.[54,56] The preparation of the mononuclear acetylacetonate complex, Pd(**126**-H)(acac), has also been reported together with the ^{1}H and ^{13}C NMR spectra of the complex.[54] In addition, the related ligand 2-*p*-tolylbenzothiazole has also been cyclopalladated,[55] as has 2-benzylbenzothiazole, the latter giving rise to complexes which incorporate a six-membered palladacycle.[100]

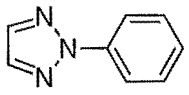


126

Upon reaction with rhodium trichloride trihydrate, **126** gives a chloro-bridged dimer, [Rh(**126**-H)$_2$Cl]$_2$, as a brown powder in poor yield. All attempts to convert this

dimeric complex into mononuclear complexes by ligand exchange with ß-diketonates gave solids which are insoluble in chloroform and, as such, were not characterised.

1.4 FIVE-MEMBERED HETEROCYCLES WITH THREE HETEROATOMS



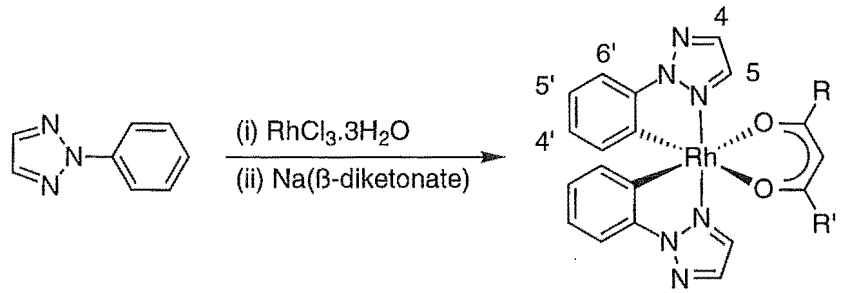
127

The first reported cyclometallation of 2-phenyl-1,2,3-triazole (**127**) was in 1975 when Allison *et al.* reported the reaction of this ligand—and several methyl- and phenyl-substituted derivatives—with lithium tetrachloropalladate.[101] The resultant chloro-bridged dimers were used to prepare selectively *ortho*-chlorinated derivatives of the 2-phenyl-1,2,3-triazoles.[101] Subsequently the mononuclear palladium acetylacetonate complex of **127** was prepared from the corresponding chloro-bridged dimer and the complex characterised by ^{1}H and ^{13}C NMR.[54]

Reaction of **127** with rhodium trichloride trihydrate in refluxing 2-methoxyethanol gave a white powder, formulated as a chloro-bridged dimer, $[Rh(\mathbf{127}\text{-}H)_2Cl]_2$, in excellent yield. This complex was characterised by ^{1}H NMR spectroscopy, the resonance at 6.13 ppm, assigned to the signal due to H-3', being significantly broadened. Ligand exchange of this complex with sodium ß-diketonates gave the corresponding mononuclear complexes—$Rh(\mathbf{127}\text{-}H)_2(acac)$ (**128**); $Rh(\mathbf{127}\text{-}H)_2(dbm)$ (**129**); and $Rh(\mathbf{127}\text{-}H)_2(bac)$ (**130**)—as white powders, in excellent yields (scheme 1.9). Diffusion of pentane vapour into chloroform solutions of the crude powders gave the complexes as analytically pure, pale yellow crystals. In addition to microanalysis, the complexes were fully characterised by ^{1}H and ^{13}C NMR spectroscopy.

Whilst assignment of the NMR spectra for all of the cyclorhodated complexes was straightforward, the chemical shifts of the protons on the triazole ring in each of the

complexes are noteworthy. Because of the symmetry of the 1,2,3-triazole ring, the signal due to both H-4 and H-5 appears at 7.82 ppm in the spectrum of the free ligand.



127

128 R=R'=CH_3
129 R=R'=C_6H_5
130 R=CH_3, R'=C_6H_5

Scheme 1.9

In the spectrum of the chloro-bridged dimer, [Rh(**127**-H)$_2$Cl]$_2$, H-4 resonates at 8.25 ppm (CIS = 0.43 ppm) and H-5, which lies above a deshielding chlorine atom, at 8.53 ppm (CIS = 0.71 ppm). In addition, the signal for H-5 shows considerable broadening, whilst that for H-4 does not. The spectrum of the acetylacetonate complex, **128**, also has two resonances corresponding to the signals for these protons, H-4 resonating at 7.97 ppm (CIS = 0.15 ppm) and H-5 at 7.90 ppm (CIS = 0.08 ppm), neither of which is broadened. In the spectrum of **129**, however, only one sharp peak, with a chemical shift of 7.92 ppm (CIS = 0.10 ppm) and an integral height corresponding to four protons, is seen, and this is assigned to the signal for both H-4 and H-5. The inequivalence of the two cyclorhodated ligands, a result of the coordination of the unsymmetrical benzoylacetonate anion, in the structure of **130** is reflected in the spectrum of the complex. Four signals—at 7.86 ppm; 7.94 ppm; and two at 7.95 ppm—are seen, and assigned to the signals due to the four protons in this complex, H-4a, H-4b, H-5a and H-5b.

1.5 CONCLUSION

In summary, this chapter has detailed the cyclorhodations of five ligands, all of which have previously been cyclometallated, and the conversion of the resultant chloro-bridged dimers to, the corresponding mononuclear ß-diketonate complexes. The preparation of three phenyloxazoles, according to literature methods, was also described, as were investigations of their complexation chemistry. This does not include any cyclometallations, however a metallation of the 5-position of the oxazole ring in 2,4-diphenyloxazole, by mercury(II), was described.

Chapter Two

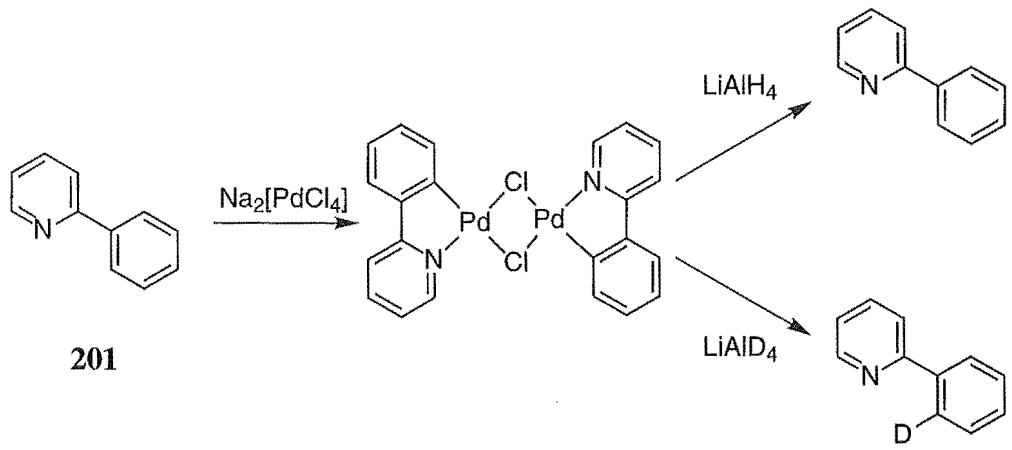
Ligands Containing Sixmembered Heterocycles and One Cyclometallation Site

2.1 INTRODUCTION

This chapter describes the preparations and reactions of ligands in which the donor is a nitrogen atom within a six-membered heterocycle. The ligands discussed are grouped according to the size of the metallocycle which they could potentially form and include a series of six related oxygen- and sulfur-containing ligands. A novel, coordinatively unsaturated complex, the product of one of the cyclorhodations herein described, is reported. Three single crystal X-ray structure determinations (two partial, one complete) are described, including a cyclorhodated complex and two mononuclear palladium coordination complexes. In addition, a number of variable temperature ^1H NMR spectra are included and a possible explanation for the observed temperature dependences proposed.

2.2 POTENTIAL FIVE-MEMBERED METALLOCYCLES

In 1968 Kasahara reported that the reaction of 2-phenylpyridine (**201**) and sodium chloropalladate gave a pale yellow solid. This compound was assigned a chloro-bridged dimeric structure on the basis of IR spectroscopy and the products obtained upon lithium aluminium hydride and deuteride reductions (scheme 2.1).[23]



201

Scheme 2.1

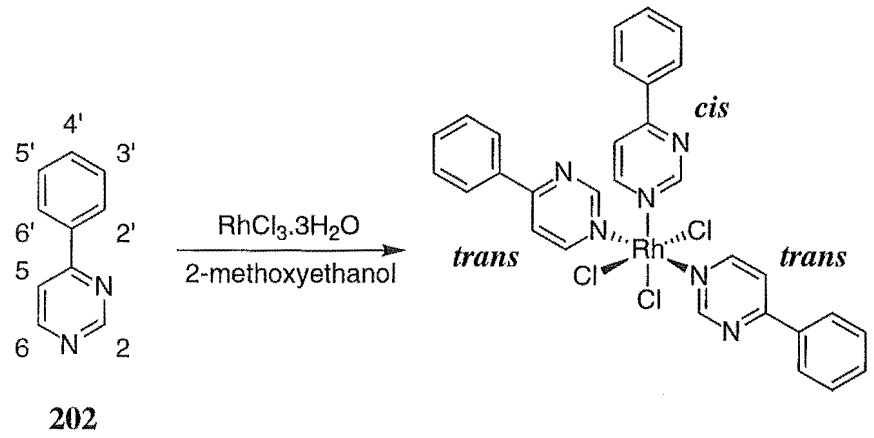
Since this first report **201** has been cyclometallated with several other metals including ruthenium, iridium and rhodium.[20] The first reported preparation of the rhodium chloro-bridged dimer, $[Rh(\mathbf{201}\text{-}H)_2Cl]_2$, was in 1971[29] and since then this

complex, and its derivatives, have been the subject of continuing interest. The cyclometallated **201** ligand is an isoelectronic analogue of the well studied N,N-donor ligand bipy and several studies have been undertaken which compare the properties—electrochemical; NMR; absorption and emission—of rhodium complexes in which bipy is replaced by cyclometallated **201** ligands.[31a,49,50,83,102-109]

Whilst several mononuclear derivatives have been prepared from $[Rh(\mathbf{201}\text{-}H)_2Cl]_2$, there have been no previous reports of any complex which has been prepared by ligand exchange of the chloro-bridged dimer with ß-diketonate anions. The corresponding cyclopalladated acetylacetonate complex, Pd(**201**-H)(acac) has previously been prepared by reaction of the chloro-bridged dimer with sodium acetylacetonate.[54]

The rhodium complex, $[Rh(\mathbf{201}\text{-}H)_2Cl]_2$, was prepared by reacting rhodium trichloride with **201** in glycerol according to the literature procedure.[50] The mononuclear rhodium ß-diketonate complexes—$Rh(\mathbf{201}\text{-}H)_2(acac)$, $Rh(\mathbf{201}\text{-}H)_2(dbm)$ and $Rh(\mathbf{201}\text{-}H)_2(bac)$—were prepared in good to excellent yields by ligand exchange of the chloro-bridged dimer with sodium ß-diketonate anions. Allowing for the inclusion of solvent molecules these monomeric complexes all returned satisfactory microanalyses and were fully characterised by ^1H and ^{13}C NMR spectroscopy.

The commercially available ligand 4-phenylpyrimidine (**202**) (scheme 2.2) has previously been cyclometallated with lithium tetrachloropalladate[110] and pentacarbonylmethylmanganese.[66] Reaction with rhodium trichloride in refluxing 2-methoxyethanol gives, after two days, a yellow powder. The ^1H NMR spectrum of this product showed that it contained non-metallated ligands—identified by the familiar coupling pattern observed for phenyl rings—in the ratio two:one. This suggested the formation of a coordination complex, $Rh(\mathbf{202})_3Cl_3$ (scheme 2.2), with meridional stereochemistry—the alternative, facial stereochemistry, would have all ligands equivalent by NMR. Following recrystallisation from dichloromethane/ether this formulation was confirmed by microanalysis.



202

Scheme 2.2*

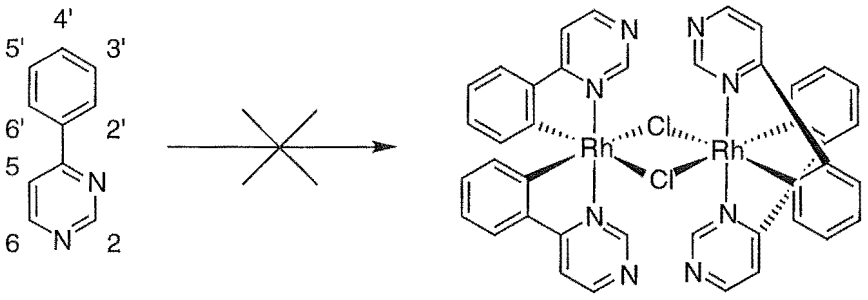
The reaction of **202** with rhodium trichloride in 2-methoxyethanol was repeated to establish whether the ligand could be cyclometallated under these conditions. After four days under reflux the suspension was filtered to give the same product, in slightly reduced yield, as that obtained above. Examination of the filtrate by ^{1}H NMR showed no evidence of cyclometallation.

The difference in the mode of coordination observed for the reaction of **202** with rhodium(III) to that observed for the reaction with palladium(II) is worthy of further discussion. Given the ease with which the ligand is cyclopalladated in 96% yield under quite mild conditions—lithium tetrachloropalladate in methanol at room temperature—it would be expected that the reaction to give the cyclorhodated analogue would readily occur. However all attempts to prepare this complex gave formation of the meridional coordination complex in which the ligand is coordinated in a monodentate fashion through N-1 as opposed to the N^3,$C^{2'}$-bidentate coordination seen in the cyclopalladated complex.

It is assumed that the difference in preferred pyrimidine donor atom results from the greater steric demands placed on the ligand by coordination to an octahedral rhodium(III) centre, relative to those by coordination to a square planar palladium(II) centre. Coordination through N-3 places the metal centre in the correct orientation for the electrophilic attack on the phenyl ring leading to the formation of the favoured

* The ligands are differentiated as *cis* and *trans* in order to facilitate unambiguous assignment of the NMR spectra, which are reported in the experimental section.

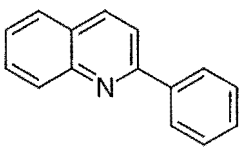
five-membered metallocycle. In the case of coordination to rhodium(III) the kinetic (steric) factors will greatly favour coordination through N-1, despite the relatively greater thermodynamic stability expected for the corresponding cyclometallated complex, $[Rh(\mathbf{202})_2Cl]_2$, within which the ligand must coordinate through the sterically less favourable N-3 atom (scheme 2.3).



202

Scheme 2.3

The preparation of the first cyclopalladated complex of 2-phenylquinoline (**203**) was reported in the same paper as that which described the first cyclopalladation of **201** (*vide supra*).[23] Reaction of **203** with sodium tetrachloropalladate in alcohol gave a yellow solid which was assigned a chloro-bridged dimeric structure, $[Pd(\mathbf{203}\text{-H})Cl]_2$, on the basis of its IR spectrum, microanalytical data and the products obtained upon reduction with lithium aluminium hydride and with lithium aluminium deuteride.[23] This known chloro-bridged dimer has subsequently been converted to the corresponding palladium acetylacetonate monomer which was then fully characterised, confirming the cyclopalladated nature of this complex.[111] Another report of the metallation of 2-phenylquinoline describes the preparation of the mercurated complex, Hg(**203**-H)Cl, and its transmetallation with tellurium tetrabromide to give the *ortho*-tellurated analogue, $Te(\mathbf{203}\text{-H})Br_3$, which was then reduced with sodium borohydride or hydrazine hydrate to give a variety of organic tellurides.[112]



203

Given the relative ease with which **203** can be cyclopalladated and the absence of reports of its cyclorhodation the reaction of this ligand with rhodium trichloride was investigated. Reaction of a solution of rhodium trichloride trihydrate and **203** in 2-methoxyethanol gave, after one day stirring at room temperature followed by one day heating under reflux, a yellow/green powder which is insoluble in $CDCl_3$, but sufficiently soluble in CD_3CN to allow the acquisition of a ^1H NMR spectrum. Examination of this spectrum, which exhibits some broadening at 23°C, showed the presence of two cyclometallated ligands—in an approximate one:two ratio—in different environments. Acquisition of a spectrum at 60°C showed that the observed broadening was due to a thermally-dependent process as this spectrum was significantly sharpened.

Recrystallisation, by the vapour diffusion of ether into an acetonitrile solution of the powder, gives a mixture of two crystal forms—well-formed orange crystals and amorphous yellow blocks—and these were manually separated by microscopic inspection.

The orange crystals were characterised by microanalysis, which returned the formulation [Rh(**203**-H)$_2$Cl].$^1/_4CH_3CN$, a stoichiometry which would be consistent with that of a chloro-bridged dimeric structure. Whilst this complex is insufficiently soluble in CD_3CN to obtain ^{13}C NMR data, the complex was able to be characterised by ^1H NMR spectroscopy. At 23°C the spectrum confirms that the broadening observed in the spectrum of the mixture is due to this complex, the signals for H-8 and H-7 being the most obviously affected. In addition, the spectrum shows that both of the ligands are in identical environments, therefore the other ligand observed as the minor component in the spectrum of the mixture must be due to another complex. At 60°C all signals are better resolved but that for H-8 still appears as a broad signal rather than, as would be expected, a doublet (figure 2.1).

Given that the crystals of the complex appeared of suitable quality for single crystal X-ray structure analysis and that the broadening observed in the ^1H NMR spectrum could not easily be accounted for, the structure of this complex was determined. The solving and partial refinement of an X-ray data set revealed, however,

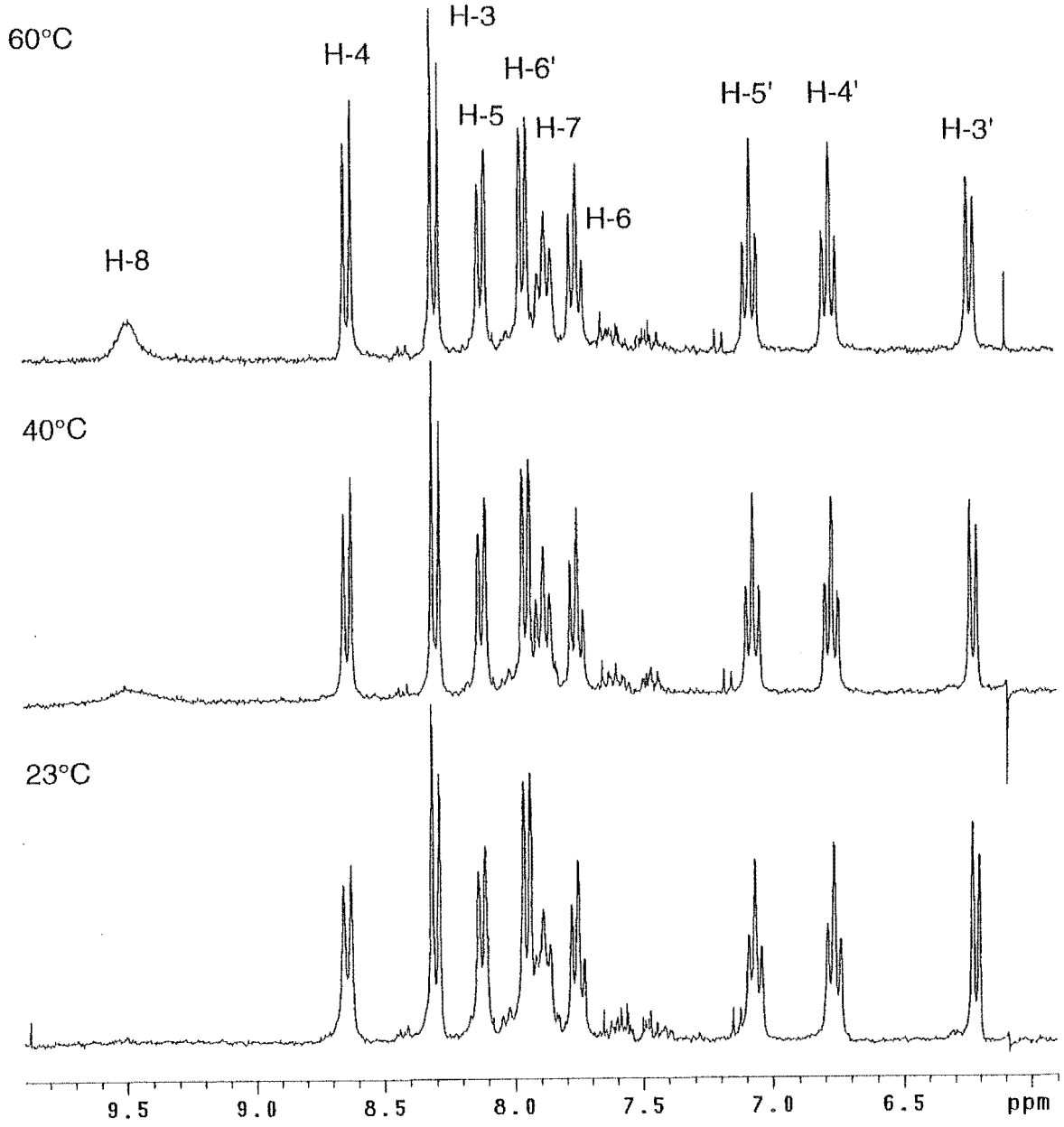


Figure 2.1 Variable temperature ^{1}H NMR spectra (CD_3CN) of [Rh(**203**-H)$_2$Cl]

that the crystals were not of the expected chloro-bridged dimer, [Rh(**203**-H)$_2$Cl]$_2$, but of another complex, Rh(**203**-H)$_2$Cl (**204**) (figure 2.2). Unfortunately, the refinement of this structure, despite several recollections on different crystals, has not produced a result of publishable quality. It is assumed that the crystals are twinned, despite this not being apparent upon examination of them under the microscope.

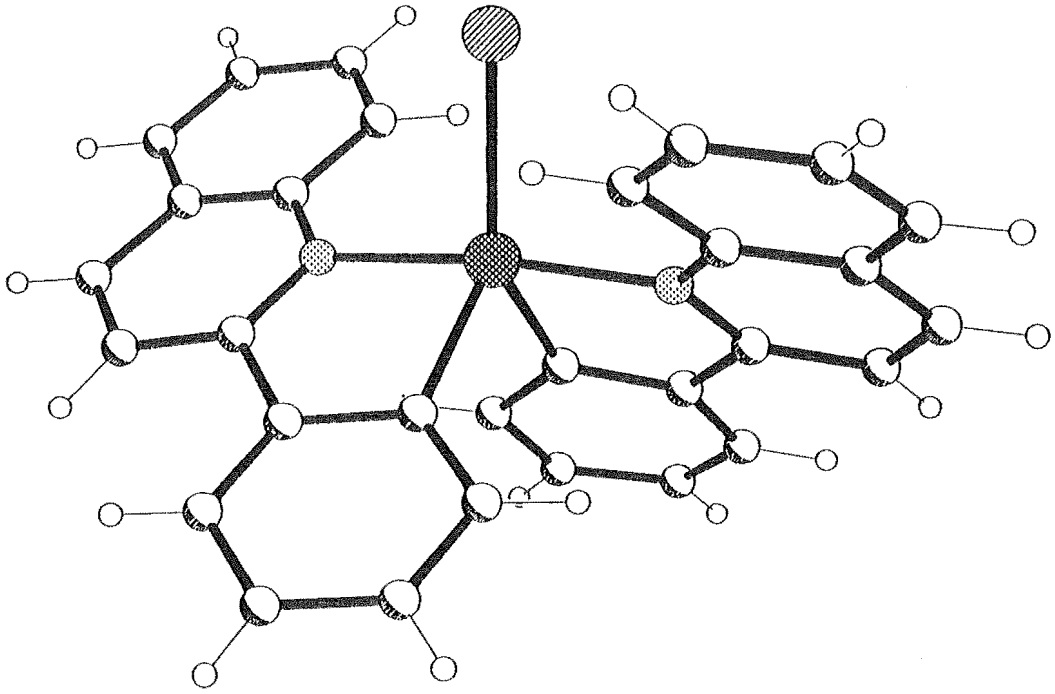
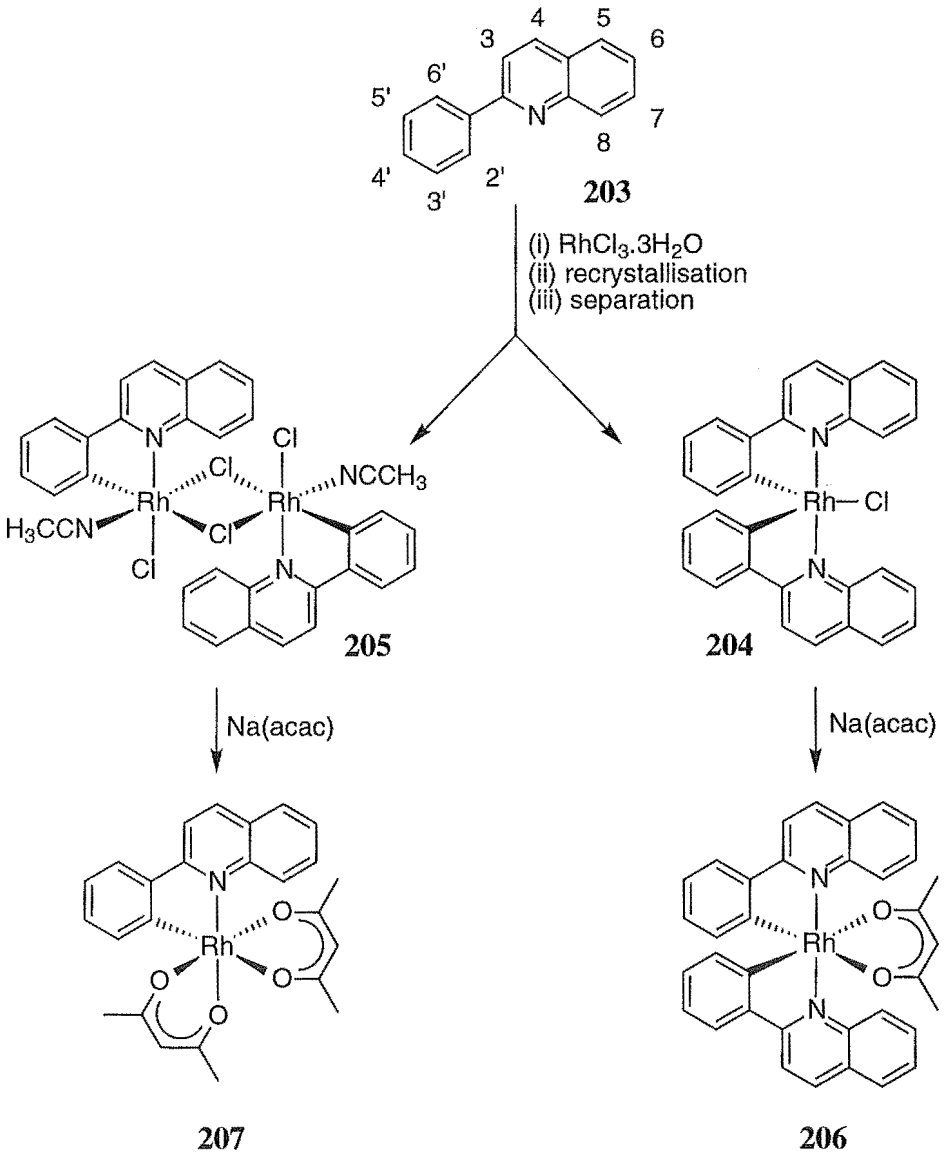


Figure 2.2 Perspective view of **204**

Despite not being suitable for publication, the structure of **204** is noteworthy. The molecule contains a coordinatively unsaturated rhodium(III) centre and two cyclometallated **203** ligands together with a single, non-bridging chlorine atom. It is interesting to contemplate the influence that the six-membered benzo-fused heterocycle has on complex formation given that, upon reaction with rhodium trichloride trihydrate under the same conditions, five-membered benzo-fused analogues give rise to chloro-bridged dimeric products (*vide supra*). The subtle alteration in the geometry of the coordination about the rhodium centre, upon expansion of the heterocycle, appears sufficient to render formation of the *meso* dimeric complex unfavourable, with respect to formation of the coordinatively unsaturated complex. Presumably, the proximity of the cyclometallated **203** ligands on adjacent rhodium(III) centres in a dimeric structure would result in such a complex being considerably strained.

The five-coordinate rhodium(III) centre in **204** is of particular interest, because a coordinatively unsaturated complex is required as an intermediate in catalytic cycles

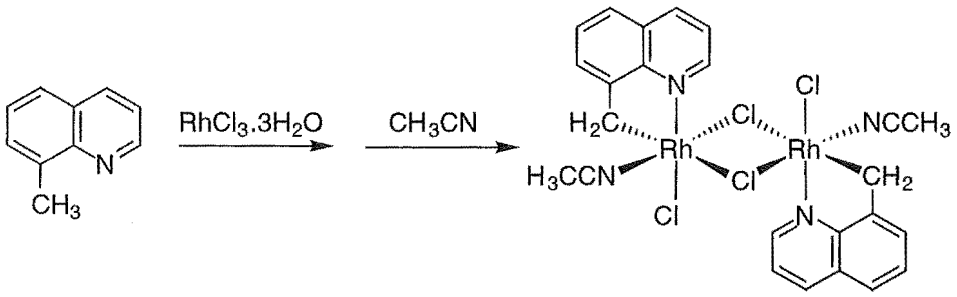
involving rhodium. Isolable examples of this type of complex are rare, the first X-ray crystal structure having been reported in 1992.[113]



Scheme 2.4

Having established the structure of the orange crystals, attention turned to determining the nature of the yellow complex obtained from the same recrystallisation. Microanalysis gave the formulation of this complex as [Rh(**203**-H)(CH_3CN)Cl_2], which is consistent with several possible structures, two of which are considered more likely. The first is a chloro-bridged dimeric structure, [Rh(**203**-H)(CH_3CN)Cl_2]$_2$—one of the many possible isomers of which is shown as **205** in scheme 2.4—in which the rhodium(III) centres are six-coordinate. The alternative structure, Rh(**203**-H)(CH_3CN)Cl_2, is monomeric and contains a coordinatively unsaturated

rhodium(III) centre. Given that, with only one ligand attached to each rhodium(III) centre, the steric interactions between the ligands on adjacent rhodium(III) atoms—and the assumed driving force to coordinative unsaturation—would be minimised, the chloro-bridged dimeric structure, **205**, is considered the most probable structure of this complex. This is analogous to the structure, proposed by Nonoyama, for the complex that results upon dissolution in CD_3CN of the adduct obtained when rhodium trichloride trihydrate is reacted with 8-methylquinoline (scheme 2.5).[114]



Scheme 2.5

As with the orange crystals, the yellow complex is not sufficiently soluble in CD_3CN to obtain ^{13}C NMR data. The ^1H NMR spectrum shows no broadening, as expected, and the presence of a cyclometallated ligand. The spectrum of this complex is very different from that of **204** (figure 2.3) as there is only one ligand attached to each rhodium(III) centre and, therefore, a lack of through-space magnetic ring current effects between ligands.

Ligand exchange, with sodium acetylacetonate, of the original mixture obtained from the reaction of **203** with rhodium trichloride trihydrate gave a yellow powder. This powder was separated by fractional crystallisation to give two complexes: Rh(**203**-H)$_2$(acac) (**206**)—which was also independently prepared from separated **204**—and Rh(**203**-H)(acac)$_2$ (**207**) (scheme 2.4). Both of these complexes are soluble in $CDCl_3$ and were characterised by ^1H and ^{13}C NMR spectroscopy and, in the case of **206**, by microanalysis.

The ^1H NMR spectrum of **206** displays none of the broadening seen in the spectrum of the corresponding complex, **204**, and all resonances are well-resolved. It is interesting to note that, whilst **204** adopts a coordinatively unsaturated structure,

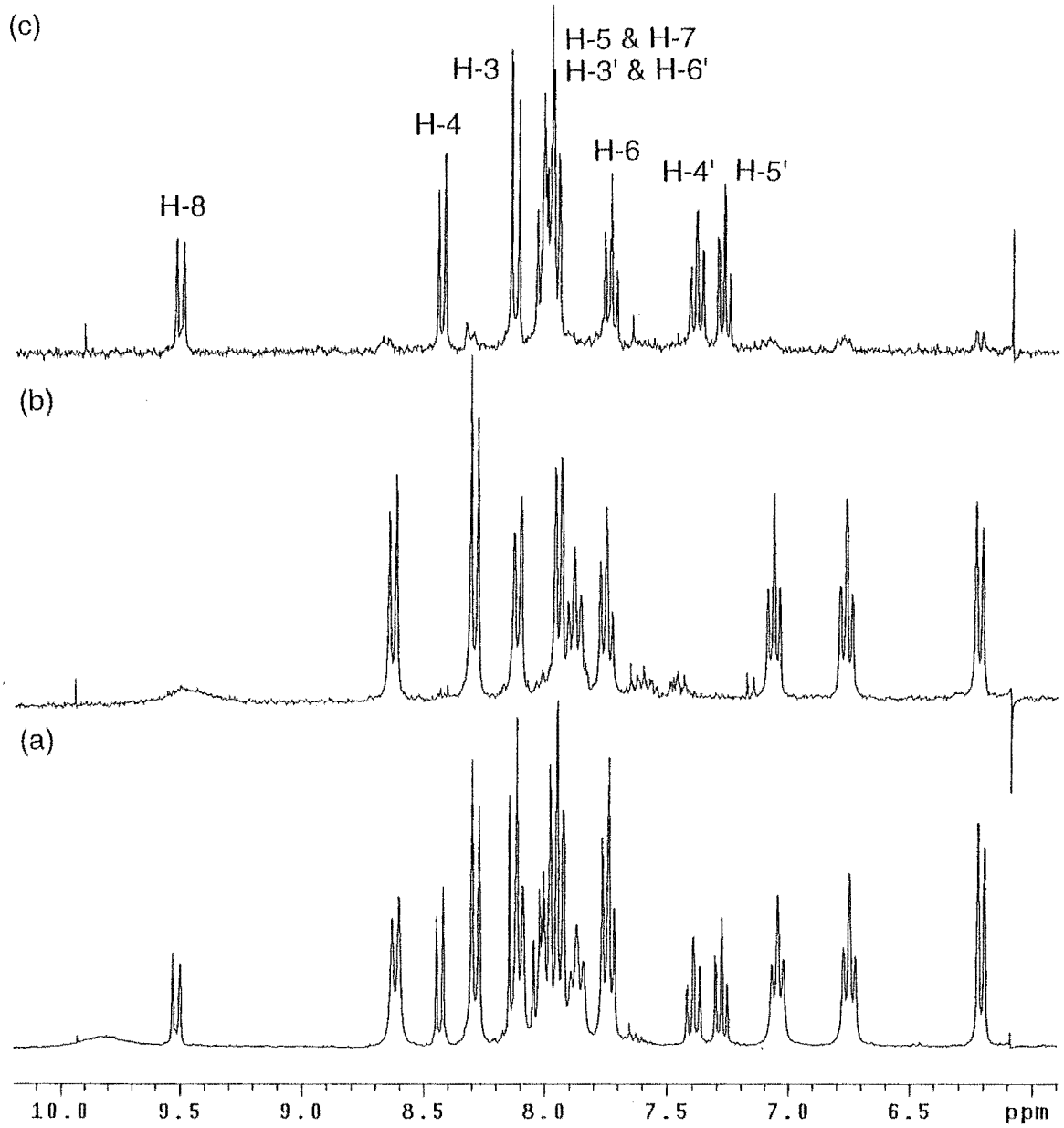


Figure 2.3 ^1H NMR spectra (CD_3CN) of: (a) the mixture from the reaction of **203** with $RhCl_3.3H_2O$; (b) **204** (see figure 2.1 for assignments); and (c) **205**

the analogous acetylacetonate complex, **206**, has a six-coordinate rhodium(III) centre. This is further evidence for the explanation given above, that the coordinatively unsaturated structure is formed because of the considerable steric strain—due to interactions between the cyclometallated ligands on the adjacent rhodium(III) centres—that would be imposed on a chloro-bridged dimeric structure. The question that remains, however, is why the vacant coordination site is not occupied by an acetonitrile molecule, given the preference that rhodium(III) displays for six-coordination.[114]

The ^{13}C NMR spectrum of **206** was easily assigned by means of an HMQC spectrum (figure 2.4) which enabled the correlations between the ^{1}H and ^{13}C signals to be seen, including the signals for H-6 and H-7, despite the proximity of their resonances in the ^{1}H NMR spectrum.

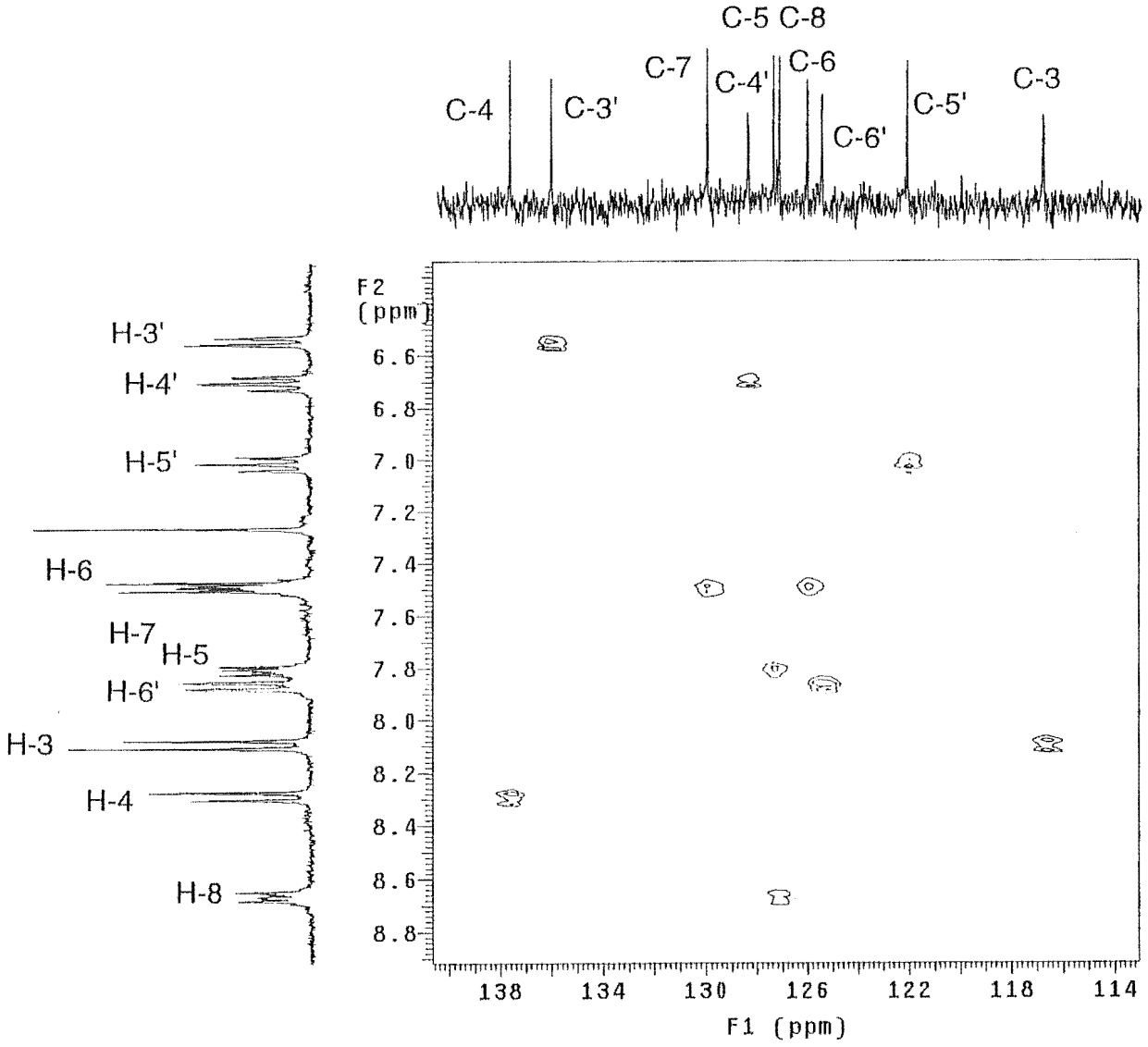
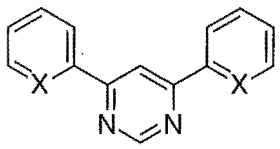


Figure 2.4 Aromatic region of the HMQC spectrum of **206**

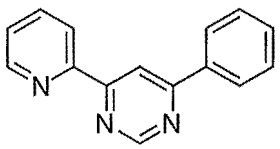
The two acac ligands in **207** are labelled $acac_a$ and $acac_b$ in the experimental section for the purposes of differentiating the signals due to each but, due to the overlap of methyl signals from each of these ligands in the ^{1}H NMR spectrum, it is not possible to completely assign the spectrum to stereochemically unique atoms. By means of NOE experiments in which the CH signals are irradiated, the signals due to each of

these ligands can be separated, but irradiation of H-8 and of H-3' gives enhancement at an overlapped resonance rather than at either of the two resolved methyl signals.

The binuclear coordination chemistry of 4,6-bis(2'-pyridyl)pyrimidine (**208**)[51] and its doubly cyclometallated analogue, 4,6-diphenylpyrimidine (**209**)[115] have been investigated. The literature on the coordination chemistry of the analogous ligand, 4-phenyl-6-(2-pyridyl)pyrimidine (**210**) is confined to a report in which the preparation of the ligand and its tris-*N*,*N*-bidentate complex with iron(II) are described.[116] In principle, this ligand offers the possibility of preparing heteronuclear complexes with each of the metals in different coordination environments, one *N*,*N*-chelated and the other cyclometallated.

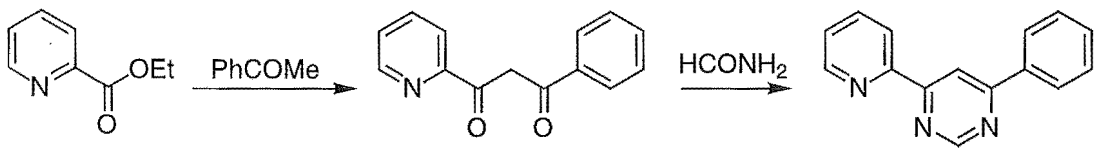


208 X=N
209 X=C



210

The ligand, **210**, was prepared by the reaction of 1-phenyl-3-(2-pyridyl)-1,3-propanedione (**211**) and formamide as previously described (scheme 2.6).[116] The required ß-diketone precursor, **211**, was prepared by the condensation of ethyl picolinate and acetophenone[117] followed by an acetic acid work-up, in a modification of the procedure previously reported.[118]

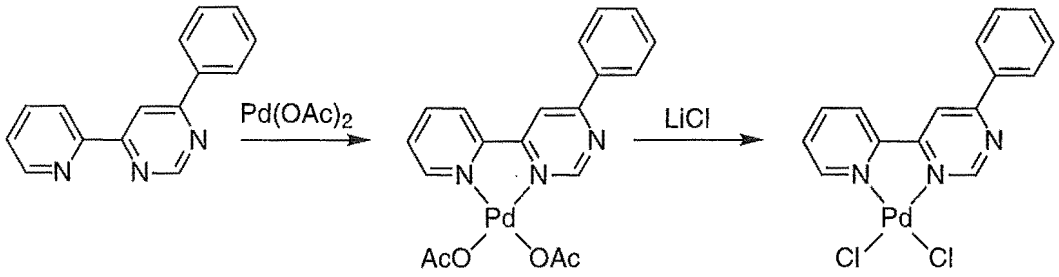


211 **210**

Scheme 2.6

Unreacted ligand is found to be the product when the black solid, obtained upon acetate-chloride exchange of the product from reaction of **210** with palladium acetate in refluxing acetic acid, is reacted with sodium acetylacetonate. This suggests that palladium acetate is not an effective metallating agent for this ligand, a conclusion that is supported by the observation that, regardless of whether the reaction is performed at

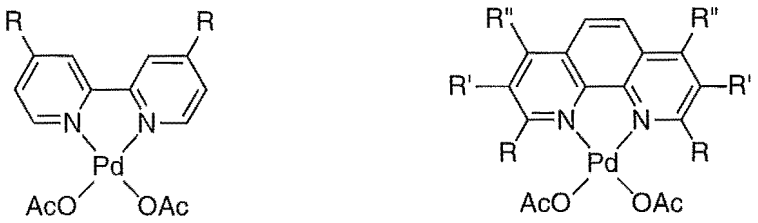
ambient or at higher temperatures, the reaction of **210** with one or two equivalents of palladium acetate in benzene gives the same product, namely the complex Pd(**210**)$(OAc)_2$ (**212**) (scheme 2.7).



210 **212** **220**

Scheme 2.7

Analogues of **212**, palladium coordination complexes containing monodentate acetate ligands, have been reported for the structurally related ligands: bipy (**213**); 4,4'-dimethyl-2,2'-bipyridine (**214**); 1,10-phenanthroline (**215**); 2,9-dimethyl-1,10-phenanthroline (**216**); 4,7-dimethyl-1,10-phenanthroline (**217**); 3,4,7,8-tetramethyl-1,10-phenanthroline (**218**) and 4,7-diphenyl-1,10-phenanthroline (**219**) (figure 2.5).[119-121]



213 R=H
214 R=Me

215 R=R'=R"=H
216 R=Me, R'=R"=H
217 R=R'=H, R"=Me
218 R=R'=R"=Me
219 R=R'=H, R"=Ph

Figure 2.5

The mode of acetate coordination in **212** was determined by correlating the carbon-oxygen stretching frequencies observed in the IR spectrum of the complex. For **212** the absorption at 1609 cm^{-1} is assigned to the asymmetric carbon-oxygen stretching frequency ($\nu_{asym}(CO_2)$), the peak at 1632 cm^{-1} being assigned to a ligand-based absorption. The frequency observed for $\nu_{asym}(CO_2)$ is an increase relative to that

observed for the parent compound, $[Pd(OAc)_2]_3$ for which $\nu_{asym}(CO_2)$=1600 cm^{-1}.[119] The frequency of the symmetric carbon-oxygen stretch, ($\nu_{sym}(CO_2)$), in the complex is observed to be 1319 cm^{-1}, a decrease relative to that observed for the parent compound for which $\nu_{sym}(CO_2)$=1427 cm^{-1}.[119] The peak at 1364 cm^{-1} is again assigned to a ligand-based absorption. The separation between the carbon-oxygen stretching frequencies, $\Delta\nu=\nu_{asym}(CO_2)-\nu_{sym}(CO_2)$, for the complex at 281 cm^{-1} is, therefore, considerably larger than that observed for the free anion in the parent compound ($\Delta\nu$=173 cm^{-1}). This observation is consistent with the assignment of the acetate coordination as being monodentate (end-on), which removes the equivalence of the two oxygen atoms, generating a pseudo-ester configuration.[121-122] The characterisation of **212** was completed with microanalysis and the assignment of its ^1H and ^{13}C NMR spectra.

Ligand exchange of **212** with lithium chloride gave the corresponding complex **220** (scheme 2.7). This complex, which is insoluble in common NMR solvents, is assumed to have monodentate chloro ligands and was characterised by microanalysis and IR spectroscopy. Reaction of **210** with lithium tetrachloropalladate gave a yellow solid which is soluble in chloroform. Acquisition of ^1H and ^{13}C NMR spectra in $CDCl_3$ showed that this complex contains two inequivalent ligands, both of which are not cyclopalladated. Extensive investigation, with a variety of techniques, did not allow characterisation of this complex and its exact formulation and structure remain unknown. Other attempts to cyclometallate **210** by reaction with mercuric acetate and with rhodium trichloride were unsuccessful. Thus, it appears that this ligand prefers to act simply as a *N,N*-bidentate ligand and does not readily undergo cyclometallation directed by the other nitrogen donor.

2.3 POTENTIAL 6-MEMBERED METALLOCYCLES

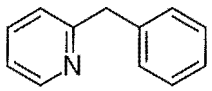
Complexes of **201** represent the classical example of a cyclometallated *N*-heterocyclic ligand with a five-membered metallocycle (figure 2.6A). The most obvious route to the preparation of analogous complexes with six-membered

metallocycles is through the insertion of a one atom spacer (denoted X) between the pyridine and phenyl rings (figure 2.6B).

A **B**

Figure 2.6

Perhaps the simplest such spacer is the methylene group, and insertion of this between the pyridine and phenyl rings gives the commercially available ligand 2-benzylpyridine (**221**).

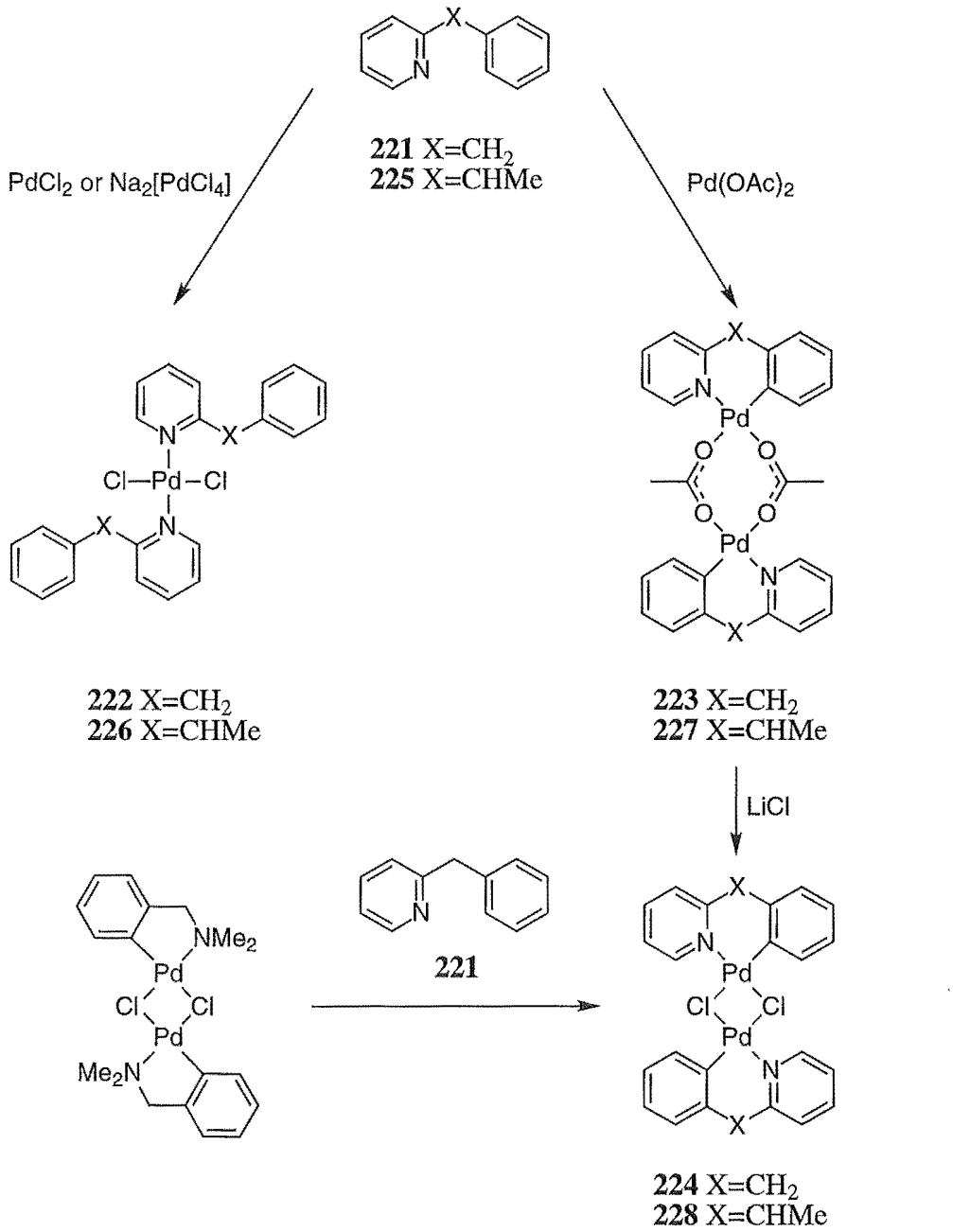


221

Reaction of **221** with palladium(II) chloride in refluxing methanol has been reported to give the coordination complex, Pd(**221**)$_2$Cl$_2$ (**222**), whilst reaction with palladium acetate in acetic acid—under reflux or at room temperature—gives the acetate-bridged dimer, [Pd(**221**-H)(OAc)]$_2$ (**223**) (scheme 2.8).[123,124] Subsequent acetate-chloride exchange gives the corresponding chloro-bridged dimer, [Pd(**221**-H)Cl]$_2$ (**224**).[123] Ligand exchange reaction of 2-benzylpyridine with the cyclopalladated *N*,*N*-dimethylbenzylamine chloro-bridged dimer also gives this complex (scheme 2.8).[125,126] Given the ease with which **224** can be prepared, it has been used as the starting material in several insertion[38a,127] and complexation[128] reactions to investigate the properties of six-membered palladacycles relative to those of their five-membered analogues.

The coordination chemistry of the structural analogue of **221**, 2-(1-methylbenzyl)pyridine (**225**), has also been reported.[129] This ligand gives a bis-coordination complex (**226**) upon reaction with sodium tetrachloropalladate and a cyclopalladated acetate-bridged dimer upon reaction with palladium acetate (**227**),

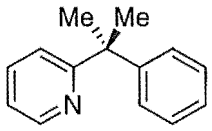
which are analogues of the complexes obtained when **221** is reacted under similar conditions (scheme 2.8).



Scheme 2.8

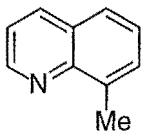
In addition to reactions with palladium(II), the reactions of **221**, **225** and their analogue, 2-(1,1-dimethylbenzyl)pyridine (**229**), with gold(III) have been reported.[30b] Upon reaction with sodium tetrachloroaurate, **221** and **225** give the coordination complexes, $AuLCl_3$, whilst **229** gives the salt, $[LH]^+[AuCl_4]^-$. Warming these compounds in aqueous acetonitrile gives the mononuclear cycloaurated complexes,

$Au(L\text{-}H)Cl_2$, which can also be prepared directly by reaction of the ligands with gold trichloride dihydrate under reflux in water.[30b]



229

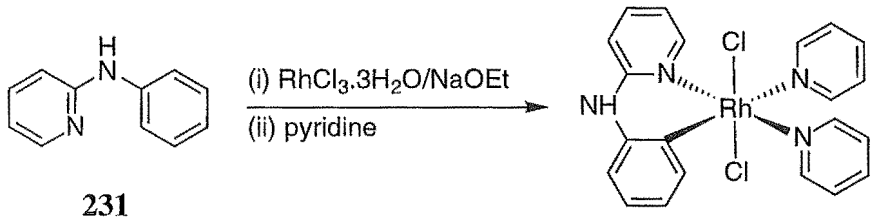
The reaction of **221** and rhodium trichloride trihydrate in 2-methoxyethanol has been reported to give the dimeric complex, $[Rh(\mathbf{221}\text{-}H)(\mathbf{221})Cl_2]_2.H_2O$, in which one of the ligands is cyclorhodated and the other coordinated solely through the pyridine nitrogen. Treatment of this complex with tertiary phosphines was reported to give mononuclear complexes, $Rh(\mathbf{221}\text{-}H)Cl_2(PR_3)_2$, which were characterised by microanalysis and IR and NMR spectroscopy, in contrast to the dimeric complex which was, due to low solubility, only characterised by microanalysis and IR spectroscopy.[130]



230

These mononuclear complexes are analogous to several reported complexes containing a single cyclorhodated ligand. Reaction of 8-methylquinoline (**230**) with rhodium trichloride trihydrate followed by treatment of the product with a variety of monodentate ligands (L) gives complexes formulated as $Rh(\mathbf{230}\text{-}H)X_2L_2$ (X = Cl or Br).[114] Of more significance to this discussion is the reaction of 2-anilinopyridine (**231**) (scheme 2.9) with rhodium trichloride trihydrate, as this ligand, like **221**, would give a six-membered metallocycle upon cyclometallation. This reaction, followed by treatment with pyridine, gives $Rh(\mathbf{231}\text{-}H)Cl_2(py)_2$, which was characterised by a single crystal X-ray structure determination (scheme 2.9).[131] Of particular note is the *trans* geometry of the chloride ligands—an observation supported by the presence of a single ν(Rh-Cl) stretch in the IR spectrum—in contrast to the *cis* geometry ascribed to the chloride ligands in $Rh(\mathbf{221}\text{-}H)Cl_2(PR_3)_2$ and $Rh(\mathbf{230}\text{-}H)X_2L_2$ on the basis of IR

spectroscopy (two ν(Rh-Cl) stretches observed) and the ^{1}H-^{31}P and ^{13}C-^{31}P couplings observed in the NMR spectra.[114,130]



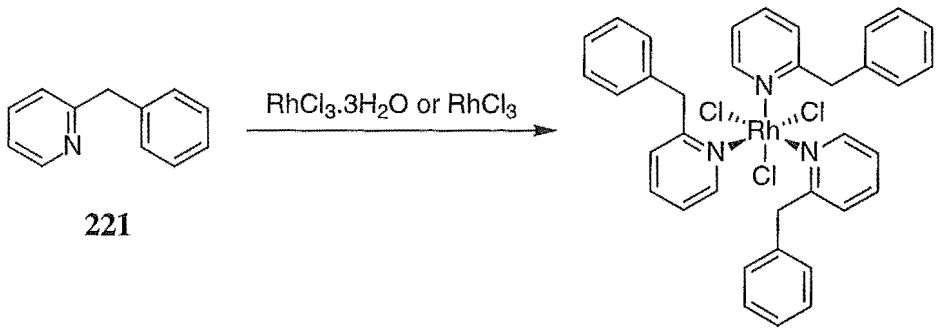
231

Scheme 2.9

In none of the reactions, with rhodium trichloride trihydrate, of **231**, **229** and **231,** is the expected chloro-bridged dimer—as reported for 2-phenylpyridine (**201**),[29] benzo[*h*]quinoline,[29] azobenzenes,[132] aromatic oximes[133] and 1-phenylpyrazole (*vide supra*)[91]—observed as the product. This has been attributed, in the case of **221** and **231**, to the fact that the ligands which give the chloro-bridged dimer consist of a conjugated system, whilst for these two ligands the moiety containing the metallated carbon atom is not conjugated with that containing the N-donor atom.[130]

As the initial step in an investigation of the formation of six-membered metallocycles, the reaction of **221** with rhodium trichloride trihydrate was carried out in 2-methoxyethanol—according to the literature procedure[130]—and in ethanol, as was the reaction with anhydrous rhodium trichloride in anhydrous ethanol. In all cases, however, the product obtained—regardless of reaction time—was not the cyclorhodated dimeric complex reported previously, but one ascribed a structure in which the ligands are monodentate, coordinated through the pyridyl nitrogen. This complex is isolated as an oil which gives an inconclusive FAB mass spectrum and is unable to be sufficiently purified to give satisfactory elemental analyses. The complex is soluble in chloroform and was characterised by ^{1}H and ^{13}C NMR spectroscopy, which demonstrated that all ligands were in equivalent environments and clearly not metallated. The microanalytical results obtained suggest that the formulation of the complex is Rh(**221**)$_3$Cl$_3$, with the equivalence of the ligands in the NMR spectra being consistent with facial stereochemistry (scheme 2.10). This is in contrast to the meridional

stereochemistry observed for the coordination complex formed when rhodium trichloride trihydrate is reacted with **202** (*vide supra*).

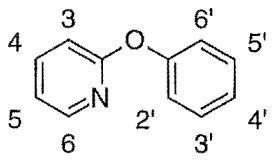


221

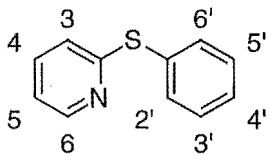
Scheme 2.10

Given that there are still relatively few reports of complexes containing six-membered metallocycles in the literature, attention was focused on potential ligands with the necessary structural features which might lead to the formation of such complexes. Using the incorporation of an appropriate one atom spacer between the two aromatic rings in **201** as a starting point for ligand design, consideration was given to compounds, analogues of **221** and **230**, whose coordination chemistry had not been investigated.

A desirable structural feature for improving the relative reactivity of such a ligand would be the incorporation of a *ortho*-activating group as the spacer. It was felt that an electron-releasing Group VI atom would fulfil this criterion, giving an increase, relative to the analogues **201** and **221**, in electron density on both the pyridyl nitrogen and the *ortho* carbons of the phenyl ring. This would increase the nucleophilicity of the former, whilst also making the latter more prone to electrophilic attack by the coordinated metal centre, thereby promoting both key steps of the postulated mechanism for cyclometallation (*vide supra*). The two compounds considered as potential ligands were, therefore, the ether, 2-phenoxypyridine (**232**), and the thioether, 2-phenylthiopyridine (**233**).



232



233

The first reported preparation of **232** was by Chichibabin in 1918, when the compound was obtained in poor yield upon the diazotisation of 2-aminopyridine in the presence of phenol.[134] The preparations of **232** reported subsequently—for investigations of its pharmacological[135] and herbicidal[136] activity—have involved the reaction of 2-bromopyridine and phenol in the presence of anhydrous potassium carbonate. This reaction was repeated to give, in good yield, the desired ether as a white crystalline solid which was fully characterised, the ^{13}C NMR assignments being in agreement with those in the literature.[137,138]

The preparation of the corresponding thioether, **233**, is most easily accomplished by the nucleophilic substitution of 2-bromo-[139] or 2-chloropyridine by thiophenolate anion in a reaction analogous to that used above to prepare **232**. Thus, reaction of 2-chloropyridine with thiophenol in the presence of triethylamine according to the literature procedure gave, after distillation, **233** as an oil in good yield.[140] Again this ligand was fully characterised, with the observed ^{1}H NMR shifts being similar to those previously reported.[141]

Having prepared and characterised the target ligands, **232** and **233**, investigation of their coordination chemistry began with their reactions with lithium tetrachloropalladate in methanol. Reaction of both ligands under these conditions gave mononuclear coordination complexes, one of which was characterised by a single crystal X-ray structure determination (*vide infra*).

Reaction of **232** with one equivalent of lithium tetrachloropalladate was expected to give the chloro-bridged dimer, $[Pd(\mathbf{232}\text{-}H)Cl]_2$. Suspicions arose however, when the yellow product from the reaction in methanol—at room temperature or under reflux—was found to be quite soluble in chloroform, this being different to other known chloro-bridged cyclopalladated dimers, which are only sparingly soluble in this solvent. The ^{1}H NMR spectrum of the complex was recorded and the signals corresponding to the four protons on the pyridine ring displayed the expected coupling pattern. However, the signals for the protons on the other ring were significantly broadened at 23°C, forming a single, relatively featureless resonance—such that the substitution of this ring

could not be ascertained—between δ = 7.23-7.47 ppm. Acquisition of spectra at increasing temperatures saw this resonance take on the familiar appearance of a monosubstituted phenyl ring, confirming that cyclopalladation had not taken place (figure 2.7)

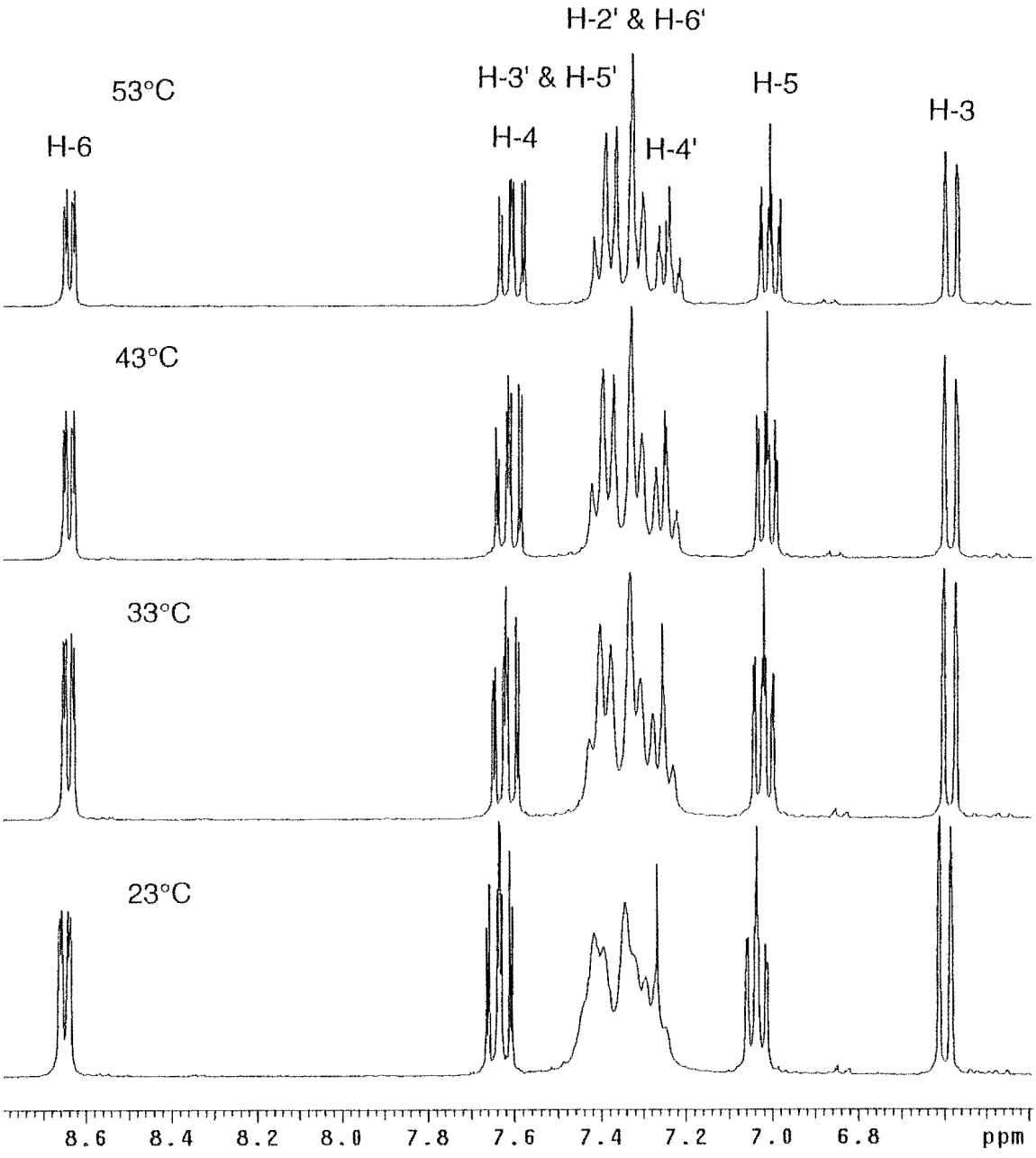


Figure 2.7 Variable temperature ^{1}H NMR spectra of the product of the reaction of **232** with lithium tetrachloropalladate

Acquisition of ^{13}C NMR spectra of the complex, both at 23°C and 53°C, showed that the carbon nuclei were also affected by the same process that led to

temperature-dependent broadening of the signals in the ^{1}H NMR spectrum. Information acquired from an HMQC experiment permitted the assignment of all resonances in the spectra.

The formulation of the complex was established by microanalysis as being Pd(**232**)$_2$Cl$_2$ (**234**)—this stoichiometry confirming that the ligands were most likely monodentate. This formulation would also be consistent with a complex in which the ligands are *N,O*-bidentate (*viz* [Pd(**232**)$_2$]Cl$_2$); however this was not considered likely as this would require the formation of an unfavourable four-membered chelate ring. Having established that the ligands in the complex were not cyclopalladated, the nature of the temperature dependent process that was leading to the observed broadening of the spectra at room temperature seemed worthy of further investigation. Initially it was felt that this was due to an agostic interaction[142] between the *ortho* protons and the palladium atom. This would lead to restricted rotation about the phenyl-oxygen bond, placing the *ortho* protons in different magnetic environments and accounting for the apparent inequivalence of their resonances at ambient temperature (figure 2.8).

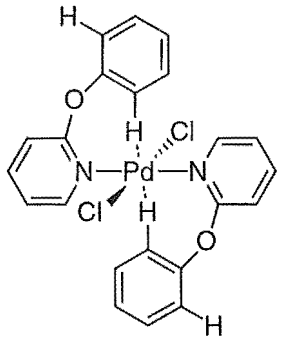


Figure 2.8

In order to characterise the complex further, and to confirm the presence of the postulated agostic interaction, it was necessary to obtain crystals for a single crystal X-ray structure determination. Diffusion of petroleum ether vapour into a chloroform solution of the complex furnished suitable crystals as orange blocks.

Crystal Structure of **234**

The palladium complex, **234**, crystallises in the monoclinic space group $P2_1/c$, the asymmetric unit of which contains half a molecule with the palladium atom sited on a centre of inversion. The two phenoxypyridine ligands are monodentate—through the pyridyl nitrogens—to the palladium atom, two chlorine atoms filling the other two coordination sites (figure 2.9).

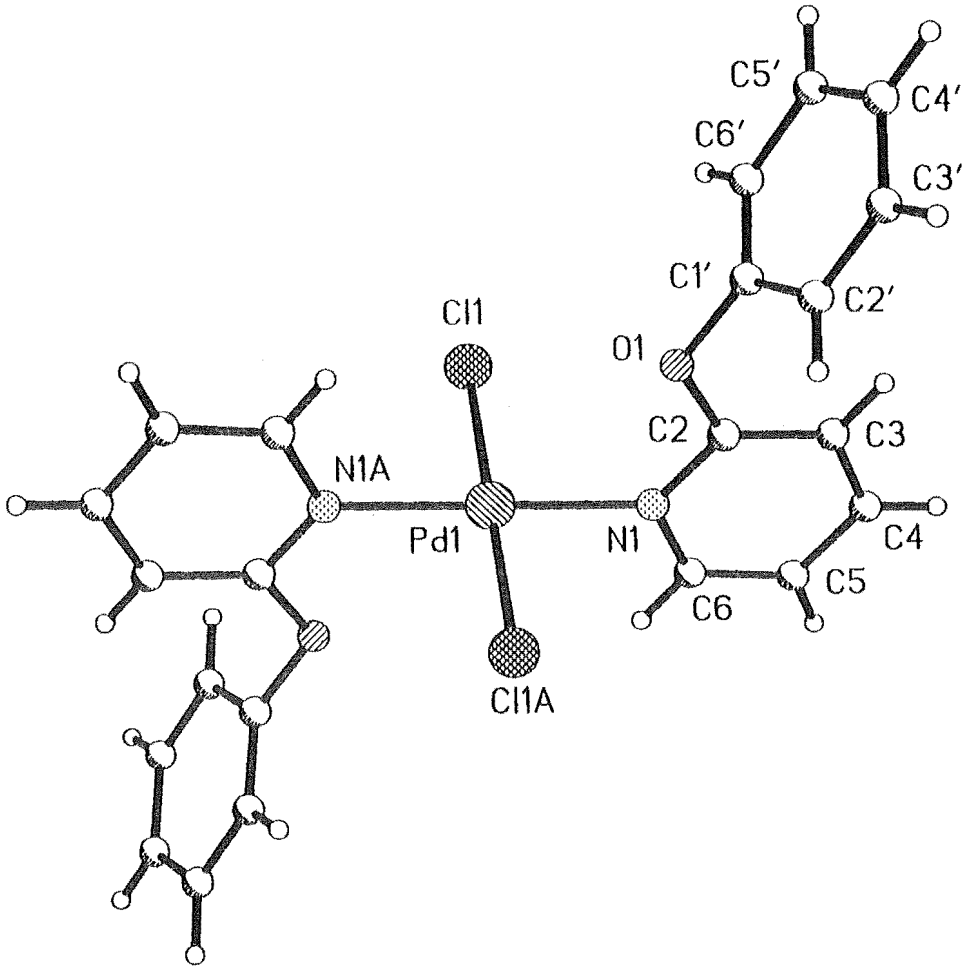


Figure 2.9 Perspective view and atom labelling of **234**. Selected bond lengths (Å) and angles (°): Pd1-N1 2.029(5), Pd1-Cl1 2.286(2), C2-O1 1.358(7), O1-C1' 1.410(7); N1-Pd1-Cl1 90.8(2), C6-N1-C2 118.5(5), C2-O1-C1' 117.5(5).

This type of complex forms the largest class of complexes obtained upon the reaction of monodentate N-donor ligands with the tetrachloropalladate anion or indeed, with palladium dichloride or bis(benzonitrile)palladium dichloride.[143] The *trans*

geometry of this complex is consistent with the observation that, in such preparations, "normally the *trans* isomer (or a mixture of isomers) is isolated."[143]

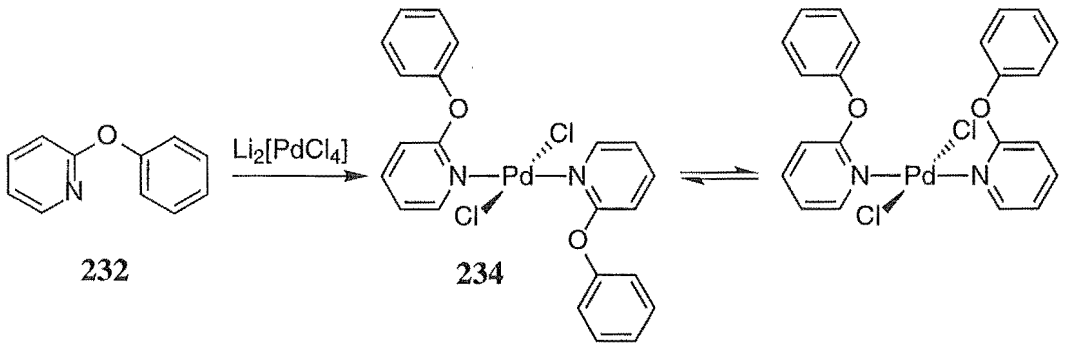
The pyridine and phenyl rings are each essentially planar with the maximum displacement from a plane being 0.018(9) Å for C6'. The meanplanes of the pyridine and phenyl rings are inclined to one another at 83.2° and are, therefore, almost orthogonal.

By virtue of the centre of inversion, the coordination about the palladium atom is crystallographically restricted to being planar and the mean plane of the pyridine ring is inclined at 100.7° to this coordination plane. The bond angles show that the coordination to the palladium is almost perfectly *square* planar with the Pd-N and Pd-Cl bonds—the lengths of which are within the expected range[144]—forming an angle of 90.82(13)°.

It might be expected that this complex would show some interaction between the oxygen atom and the palladium centre; however, the distance between them, at 2.999(7) Å, precludes such an interaction. The structure has no unusually short intermolecular distances between non-hydrogen atoms with the shortest observed being > 3.4 Å. The molecular packing is best described as involving the formation of channels of phenyl rings stacked along the *b* axis.

The crystal structure analysis detailed above, suggests a possible explanation for the temperature dependent process affecting the NMR spectra. Rather than being due to an agostic interaction between the *ortho* protons and the palladium atom (figure 2.8), the observed broadening is thought to result from the interchange between *syn* and *anti* rotamers, as depicted in scheme 2.11. This is the same phenomenon that was observed for $Pd(\mathbf{111})_2Cl_2$ (*vide supra*). In the latter complex, the interchange between rotamers is observed to be slow on the NMR timescale, such that both rotamers are observed, whilst for **234** the interchange is obviously faster, as a time-averaged spectrum is observed. This is attributed to the energetic barrier between the two rotamers in **234**

being somewhat less than in Pd(**111**)$_2$Cl$_2$. The barrier is presumed due to the steric interactions that result during the 180° rotation, about the palladium-nitrogen bond, required to effect the interchange. Upon such a rotation in **234**, only one phenoxy group must pass through the palladium coordination plane, and in the process a pyridine-oxygen bond eclipses a palladium-chlorine bond. In Pd(**111**)$_2$Cl$_2$, the equivalent rotation requires two phenyl groups to pass through the plane and, consequently, two oxazole-phenyl bonds eclipse two palladium-chlorine bonds—the latter a much more energetically demanding process than the former. The formation of rotamers of this type, and the subsequent effects on the ^{13}C NMR spectra of the complexes, has been previously proposed for *trans*-dichloropalladium complexes of N-coordinated vitamin B_6 compounds.[145] It is perhaps surprising, given how readily such palladium coordination complexes are formed, that reports of this type of isomerism do not appear more frequently.



Scheme 2.11

Reaction of the analogous thioether, **233**, with lithium tetrachloropalladate gave a pale yellow solid which is sparingly soluble in chloroform. Acquisition of a ^{1}H NMR spectrum in $CDCl_3$ (figure 2.10) showed that the product appears to be a mixture of two complexes in an approximate one:two ratio, the relative composition of which remains unchanged after several days in solution. In addition, the appearance of the spectrum does not change with increasing temperature.

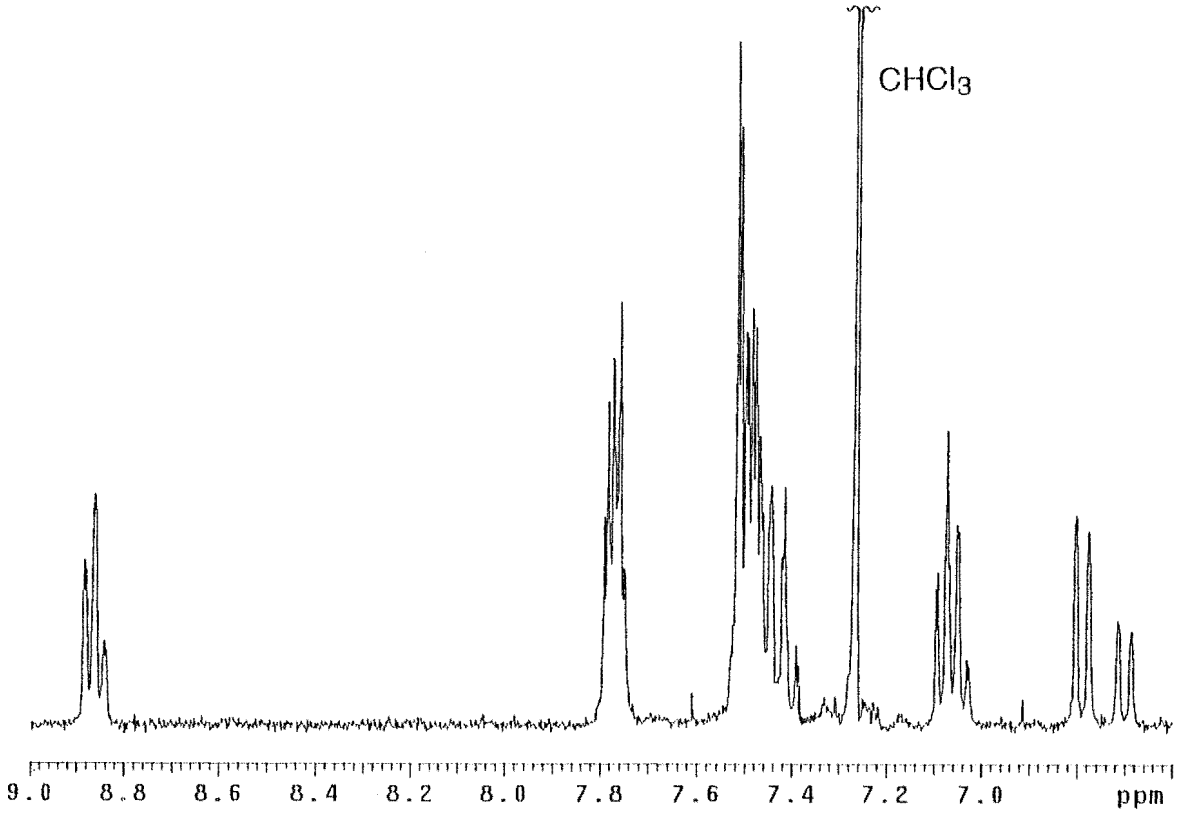
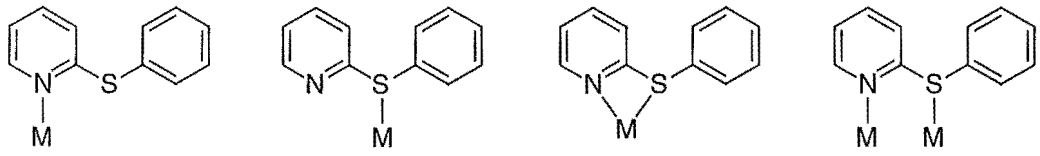


Figure 2.10 ^{1}H NMR spectrum of the product obtained upon reaction of **233** with lithium tetrachloropalladate

The use of 1D-TOCSY experiments enabled the isolation of the two different pyridyl spin systems, the signals assigned to H-3 in these systems—at δ = 6.70 ppm (minor component) and 6.79 ppm (major component)—showing the greatest separation of the pairs of related signals, with resonances separated by 0.09 ppm. The two separate phenyl ring spin systems were unable to be distinguished due to the proximity of their resonances but the size of the integral of the peak assigned to the resonance due to the *ortho* protons confirmed the non-cyclometallated nature of the complexes.

There are four possible non-cyclometallated coordination modes for this ligand: monodentate through the pyridyl nitrogen (A) or through the sulfur atom (B); mononuclear chelation through these two atoms (C); or a binuclear bidentate mode in which the ligand bridges two separate palladium centres (D) (figure 2.11). Given the similarity in chemical shifts for their equivalent positions, it is assumed that the ligands in the two complexes in the mixture adopt the same mode of coordination.



A B C D

Figure 2.11

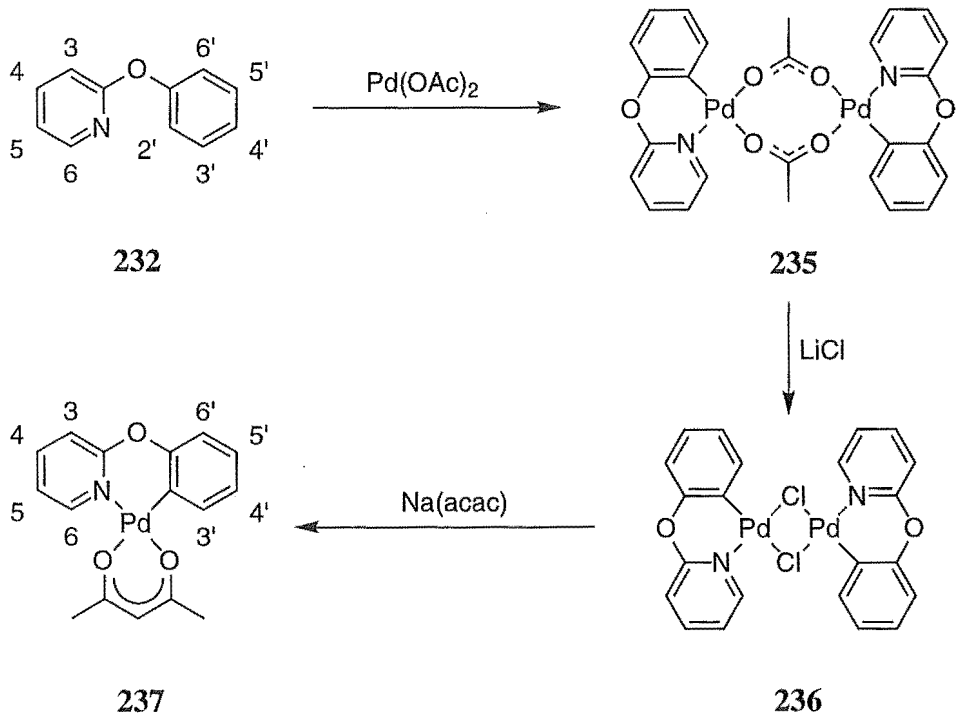
Whilst a satisfactory microanalysis of the complex could not be obtained, even after repeated attempts at recrystallisation, those obtained are consistent with the formulation of the complex as being Pd(**233**)$_2$Cl$_2$—a stoichiometry which discounts the bridging mode of coordination, D (figure 2.11). Unfortunately, these recrystallisations also failed to give crystals of a quality suitable for an X-ray crystal structure determination.

It might be expected that palladium(II) as a 'soft' metal would preferentially coordinate to **233** through sulfur, rather than nitrogen. However, in complexes where the metal can bind to a harder or softer atom in a given ligand, it has been observed that "steric effects tend to determine the result."[144] Also, due to electronic factors, the sulfur atom in **233** is somewhat harder than usual whilst the nitrogen is concomitantly softer. The similarity in CIS values observed for this complex and those observed for the analogous, crystallographically characterised complex **234** (*vide supra*), suggests that the ligands in both complexes are coordinated in a monodentate fashion through the pyridyl nitrogen.

Having established the mode of coordination and stoichiometry of the complex, one question remains unanswered: what are the structures of the two different complexes observed in the reaction between **233** and lithium tetrachloropalladate? Using the information discussed above, it is thought that the product is a mixture of *syn*- and *anti*-Pd(**233**)$_2$Cl$_2$ rotamers, with the *anti* rotamer thought to be the lower energy conformation and, therefore, the major component. The observed difference in the temperature dependences of the ^{1}H NMR spectra of the product formed upon reaction of the analogous ligands **232** and **233** is attributed to the relative sizes of the atoms separating the pyridyl and phenyl rings. The relatively larger sulfur atom is thought to

lead to larger steric interactions upon a 180° rotation about the palladium-nitrogen bond. Alternatively, although not observed for the oxygen atoms in **234,** interaction between the palladium and ligand sulfur atoms—given the donor preferences of palladium(II)—may account, either wholly or in conjunction with the respective size differences, for the observed temperature dependences.

Having established that reaction of **232** or **233** with lithium tetrachloropalladate gives coordination complexes, their reactions with palladium acetate were investigated. Reaction of **232** with palladium acetate in acetic acid at room temperature—the same conditions used to cyclometallate **221**[124]—gave, after stirring for one day, a pale yellow precipitate which shows appreciable solubility in chloroform. Using 1D-TOCSY and HMQC experiments it was possible to unequivocally establish that this product is a cyclopalladated acetate-bridged dimer (**235**) (scheme 2.12). This was recrystallised by the diffusion of petroleum ether vapour into a chloroform solution to give the complex as analytically pure yellow blocks, the characterisation of which was completed with the recording of its IR spectrum.



232 **235** **236** **237**

Scheme 2.12

Ligand metathesis of **235** with excess lithium chloride gave the chloro-bridged dimer, **236**, as an analytically pure, pale yellow solid which is largely insoluble in

common NMR solvents. Additional characterisation of this complex was, therefore, restricted to IR spectroscopy. Reaction of **236** with sodium acetylacetonate gave **237**, the desired mononuclear acetylacetonate complex, as an analytically pure white solid in moderate yield. The complex was completely characterised by means of IR and ^{1}H and ^{13}C NMR spectroscopy.

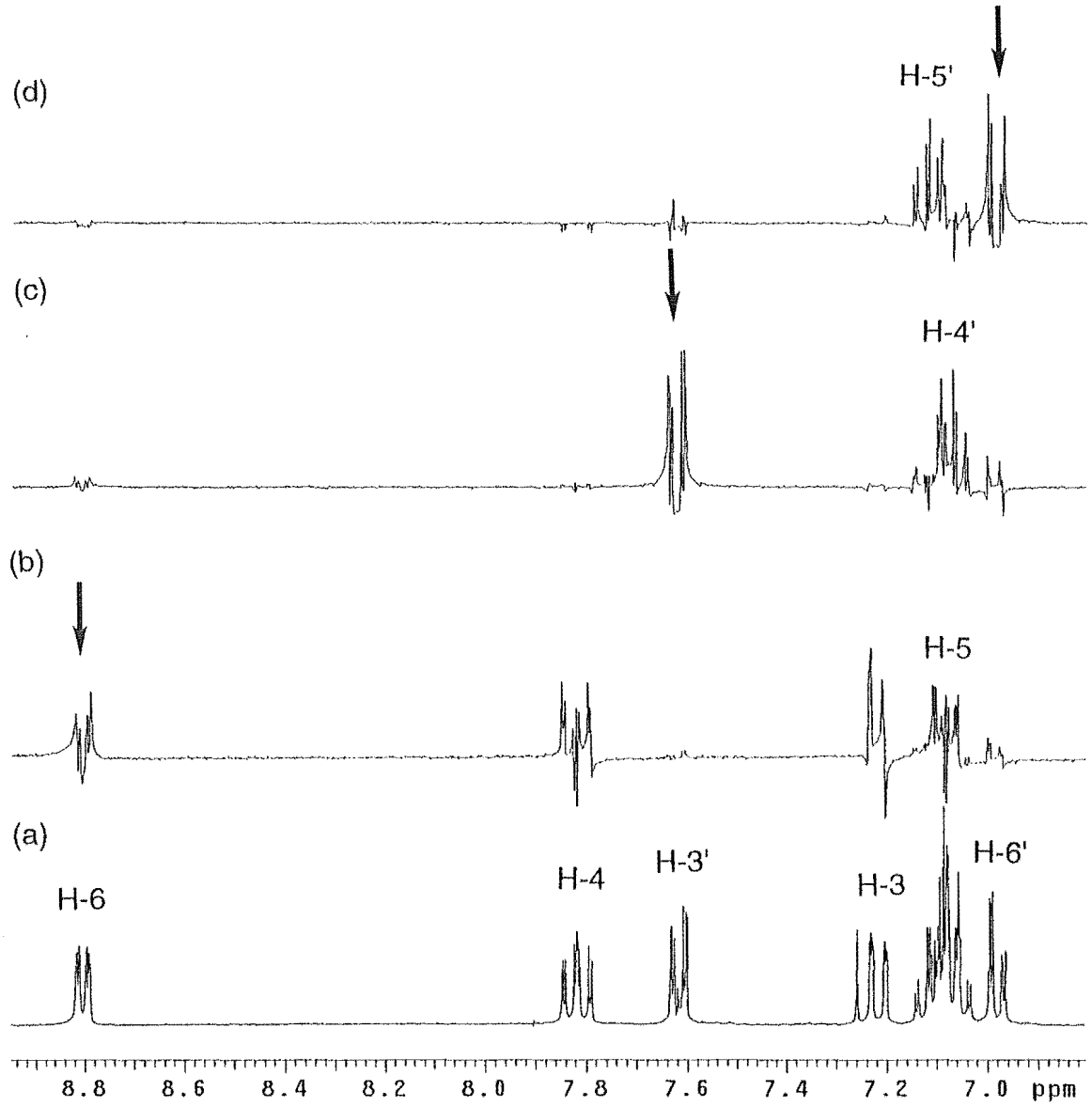


Figure 2.12 (a) Aromatic region of the ^{1}H NMR spectrum of **237**

(b) 1D-TOCSY experiment irradiating H-6

(c) 1D-TOCSY experiment irradiating H-3'

(d) 1D-TOCSY experiment irradiating H-6'

Assignment of the ^{1}H NMR spectrum (figure 2.12a) was complicated by the overlap of the resonances for H-5, H-4' and H-5'. These signals could be separated however, by the use of 1D-TOCSY experiments. Irradiation of the doublet at 8.81 ppm (assigned to H-6) provided the entry into the pyridyl ring spin system allowing the assignment of the triplet at 7.08 ppm as being the resonance due to H-5 (figure 2.12b). The doublets at 6.98 ppm (assigned to H-6') and at 7.62 ppm (assigned to H-3') offered two entries into the spin system of the cyclopalladated ring. Irradiation of the signal for H-3' at 7.62 ppm with a short mixing time (figure 2.12c), resulted in magnetisation transfer only to the adjacent proton, H-4', at 7.06 ppm.. Similarly, irradiation of the signal for H-6' at 6.98 ppm (figure 2.12d) allowed assignment of the adjacent proton H-5' at 7.12 ppm.

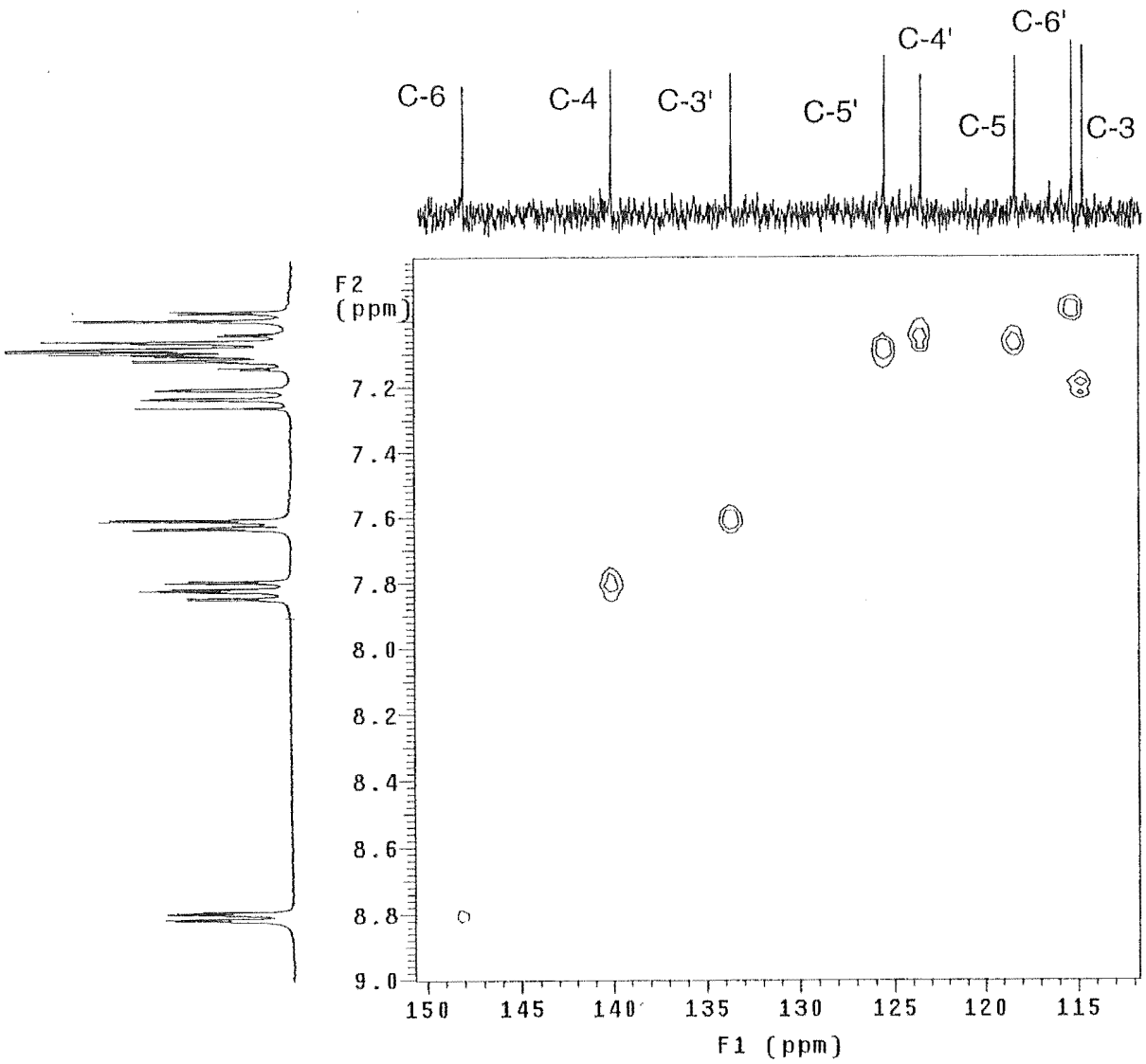
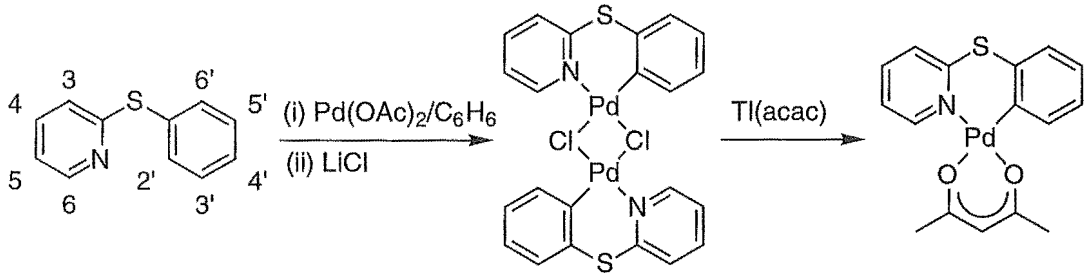


Figure 2.13 Aromatic region of the HMQC spectrum of **237**

Having fully assigned all resonances in the ^{1}H NMR spectrum of **237**, assignment of the ^{13}C NMR spectrum of the complex was made straightforward by the use of an HMQC experiment which showed individual correlations between all of the resonances in the ^{13}C NMR spectrum and the assigned resonances in the ^{1}H NMR spectrum (figure 2.13).

Reaction of the corresponding thioether, **233**, with palladium acetate in acetic acid at room temperature, or under reflux, failed to produce the desired acetate-bridged dimer. Having established that the reaction, under nitrogen, in benzene could be used to cyclopalladate ligands that failed to metallate with palladium acetate in acetic acid (*vide infra*), **233** was reacted under these conditions to give, following acetate-chloride exchange, a cyclopalladated chloro-bridged dimer, **238** (scheme 2.13), as an orange solid. This complex is insoluble in common NMR solvents and was, therefore, characterised only by IR spectroscopy.



233 **238** **239**

Scheme 2.13

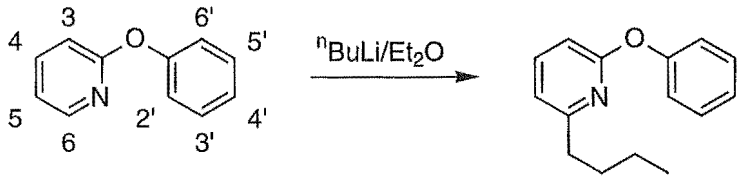
Ligand exchange of **238** with thallium acetylacetonate gave the monomeric palladium acetylacetonate complex, **239**, in relatively poor yield (scheme 2.13). Analytically pure, well-formed orange crystals were obtained following diffusion of pentane vapour into a chloroform solution of the complex. These crystals were completely characterised by means of IR and ^{1}H and ^{13}C NMR spectroscopy.

Having cyclopalladated both **232** and **233**, their reactions with rhodium trichloride, in 2-methoxyethanol and in ethanol, were investigated. None of these reactions produced cyclorhodated complexes and, in the case of **232** in 2-methoxyethanol, the apparent reduction of rhodium(III) to rhodium metal—indicated

by the formation of a solid silvery coating on the inside of the reaction vessel—was observed. Reactions with other metal ions, mercury(II) and platinum(II) for example, also did not yield cyclometallated complexes.

The presence of a nitrogen-containing heterocycle offers the possibility, through a lithiation reaction, of selectively *ortho* activating an adjacent aromatic ring.[146-148] The subsequent transmetallation of this lithiated ligand with a variety of metal ions can then be used to prepare a desired cyclometallated complex. This methodology has been used to prepare cyclometallated derivatives of a number of different heterocycles with different metal ions, for example: copper(I),[60] mercury(II)[61,62] and tin(IV)[149,150] with oxazolines; palladium(II)[150] and platinum(II)[97] with pyrazoles; palladium(II),[97,151] platinum(II)[151,152] and tin(IV)[149] with pyridines; and palladium(II) and platinum(II) with quinolines.[151]

Given the failure of direct reaction to produce cyclometallated complexes of **232** with any metal other than palladium, it was thought that lithiation and transmetallation might offer the possibility to prepare such complexes. In addition, **232**, was thought to be a good model compound for similar reactions of two diazine bis-ethers (*vide infra*). Rather than giving the desired lithiated compound, reaction of **232** with n-butyllithium in ether—in the presence or absence of TMEDA[153]—gave the hitherto unknown butylated compound, 6-butyl-2-phenoxypyridine (**240**) as a yellow oil which was characterised by mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy (scheme 2.14).



232 **240**

Scheme 2.14

2.4 POTENTIAL 7-MEMBERED METALLOCYCLES

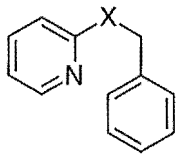
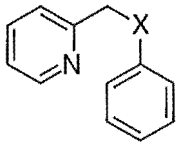
With the limited success of the strategy outlined above for the preparation of complexes containing a six-membered metallocycle, attention turned to the possibility of extending the application of this to the preparation of complexes with larger metallocycles. Just as **201**—which forms five-membered metallocycles—was used as the prototype ligand for the insertion of a one-atom spacer (denoted X) to give **232** and **233**, these two ligands—which form six-membered metallocycles—could be used as prototypes for the insertion of an additional one-atom spacer (denoted Y) to give ligands which could, in theory, form complexes which incorporate a seven-membered metallocycle (figure 2.14).

Reports of complexes which incorporate a seven-membered palladacycle are rare. Of those that have been reported, few have been prepared *via* direct cyclometallation reactions, the majority having been prepared *via* the insertion of various molecules into the palladium-carbon bond of cyclopalladated precursors.[38e,154-158]

A **B**

Figure 2.14

There are two positions into which a one-atom spacer might be inserted into the structures of **232** and **233**—adjacent to the pyridine ring (figure 2.14A) or adjacent to the phenyl ring (figure 2.14B)—and, therefore, four possible ligands arise from the insertion of such a spacer. Considering perhaps the simplest such spacer, a methylene group, the four potential ligands are: 2-phenylmethoxypyridine (**241**); 2-phenoxymethylpyridine (**242**); 2-[(phenylmethyl)thio]pyridine (**243**) and 2-[(phenylthio)methyl]pyridine (**244**).

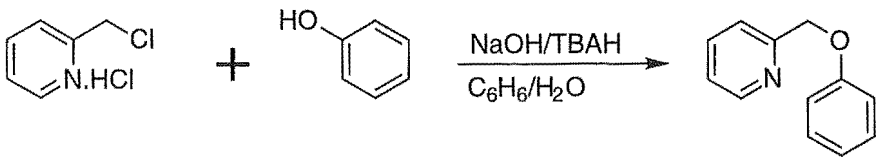



241 X=O
243 X=S

242 X=O
244 X=S

Whilst these four compounds have all been previously reported in the literature, a search revealed that the only previous report of the investigation of their coordination chemistry was a paper in which the products of reactions of **244** with potassium tetrachloroplatinate were described.[159] Reaction of these two compounds in water gives the insoluble salt, $[Pt(\mathbf{244})_2][PtCl_4]$, whilst the same reaction in DMF gives the soluble complex, *cis*-$[Pt(\mathbf{244})Cl_2]$ and, in both complexes, the ligand adopts a bidentate mode of coordination with both the pyridyl nitrogen and the sulfur acting as donor atoms.[159]

Two reactions have previously led to the synthesis of **242**, namely: (i) the reaction of phenol with 2-(chloromethyl)pyridine in the presence of sodium ethoxide;[160] and (ii) the reaction of 2-bromopyridine with sodium benzyloxide in benzyl alcohol.[161] The first of these reactions gives a product which is significantly contaminated by 2-ethoxymethylpyridine and, in the absence of a full procedure, or yields, for the latter, it was decided to investigate the preparation of this ligand by the reaction of 2-(chloromethyl)pyridine hydrochloride with phenol under phase transfer catalysed conditions. Thus, equimolar quantities of these two reagents were refluxed in benzene and aqueous sodium hydroxide with a catalytic amount of tetrabutylammonium hydroxide (TBAH) (scheme 2.15). This gave, after work-up and distillation, the desired

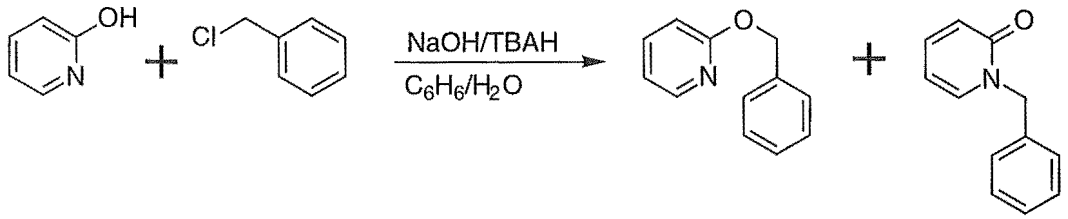


242

Scheme 2.15

compound, **242**, in good yield. The ligand was completely characterised by ^{1}H and ^{13}C NMR spectroscopy and by mass spectrometry.

Given the success of phase transfer catalysis in the preparation of **242**, the synthesis of **241** under the same conditions was attempted. Therefore equimolar quantities of 2-hydroxypyridine (2(1*H*)-pyridone) and benzyl chloride were refluxed with a catalytic amount of TBAH in benzene and aqueous sodium hydroxide. ^{1}H NMR analysis of the crude solid from this reaction suggested that it was not the expected O-alkylated compound, **241**—which is a liquid at room temperature—but was, instead, the N-alkylated product 1-benzyl-2(1*H*)-pyridone (**245**) (scheme 2.16).[162,163] Following recrystallisation of the crude solid from petroleum ether, this was confirmed by a melting point determination. In addition, **245** was also characterised by IR and ^{13}C NMR spectroscopy and by mass spectrometry. Closer examination of the ^{1}H NMR of the crude solid showed that **241** was present. The ratio of N-alkylation: O-alkylation was determined as 97:3, which differs from the 84:16 ratio previously reported for the reaction performed under similar conditions with tetrabutylammonium bromide as the catalyst.[164]

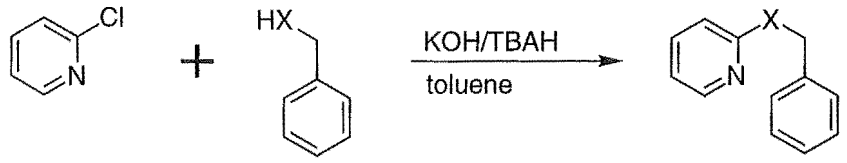


3% **241** 97% **245**

Scheme 2.16

Previously, **241** has been prepared under phase transfer conditions by the reaction, in toluene, of 2-chloropyridine and benzyl alcohol in the presence of potassium hydroxide with 18-crown-6 as the catalyst.[165] This reaction was repeated using TBAH in place of 18-crown-6 and the desired compound was isolated, after distillation, as an oil in good yield (scheme 2.17). The observed ^{1}H NMR and mass spectra of this ligand were in agreement with those previously reported and full characterisation was completed with the acquisition of a ^{13}C NMR spectrum.

There are several reports in the literature concerning the preparation of **243**, the sulfur analogue of **241**.[166-169] The most convenient method for the preparation of this compound is the reaction of 2-mercaptopyridine with benzyl chloride either in acetone[166] or under phase transfer conditions,[167,168] the latter method giving lower published yields.



241 X=O
243 X=S

Scheme 2.17

Given the ease with which the ether, **241**, was prepared by the phase transfer reaction of 2-chloropyridine and benzyl alcohol (*vide supra*), it was decided to investigate whether a similar reaction between 2-chloropyridine and benzyl mercaptan would give the analogous thioether, **243**. Thus, reaction, in toluene, of 2-chloropyridine and benzyl mercaptan in the presence of potassium hydroxide with TBAH as the catalyst gave the desired compound in satisfactory yield (scheme 2.17). The compound was fully characterised by IR and ^{1}H and ^{13}C NMR spectroscopy and by mass spectrometry. The chemical shifts observed in the ^{1}H NMR spectrum and the fragmentation pattern observed in the mass spectrum are in close agreement with those previously reported.[167,168]

The final compound in this series, **244**, was synthesised according to a literature procedure.[159,170] Thus, reaction of sodium thiophenoxide and 2-chloromethylpyridine hydrochloride gave the desired compound which was fully characterised by IR and ^{1}H and ^{13}C NMR spectroscopy and by mass spectrometry. The alternative preparation—in a paper which investigates the compound's anti-inflammatory properties—involves the reaction of 2-(hydroxymethyl)pyridine and thiophenol in refluxing hydrobromic acid and this was not repeated as it gives lower reported yields.[171]

Having prepared and characterised the four target ligands, investigation of their coordination chemistry commenced with their reactions with lithium tetrachloropalladate in methanol at room temperature. Reaction of **241** with lithium tetrachloropalladate was carried out without stirring of the reaction mixture, in the hope that this might give the direct deposition of crystalline product. This was not the case and the reaction gave a yellow powder, which has limited solubility in chloroform. An IR spectrum of the solid was recorded and microanalysis gave the formulation $Pd(\mathbf{241})_2Cl_2$ (**246**), which suggested the formation of a coordination complex, assumed to have *trans* stereochemistry.

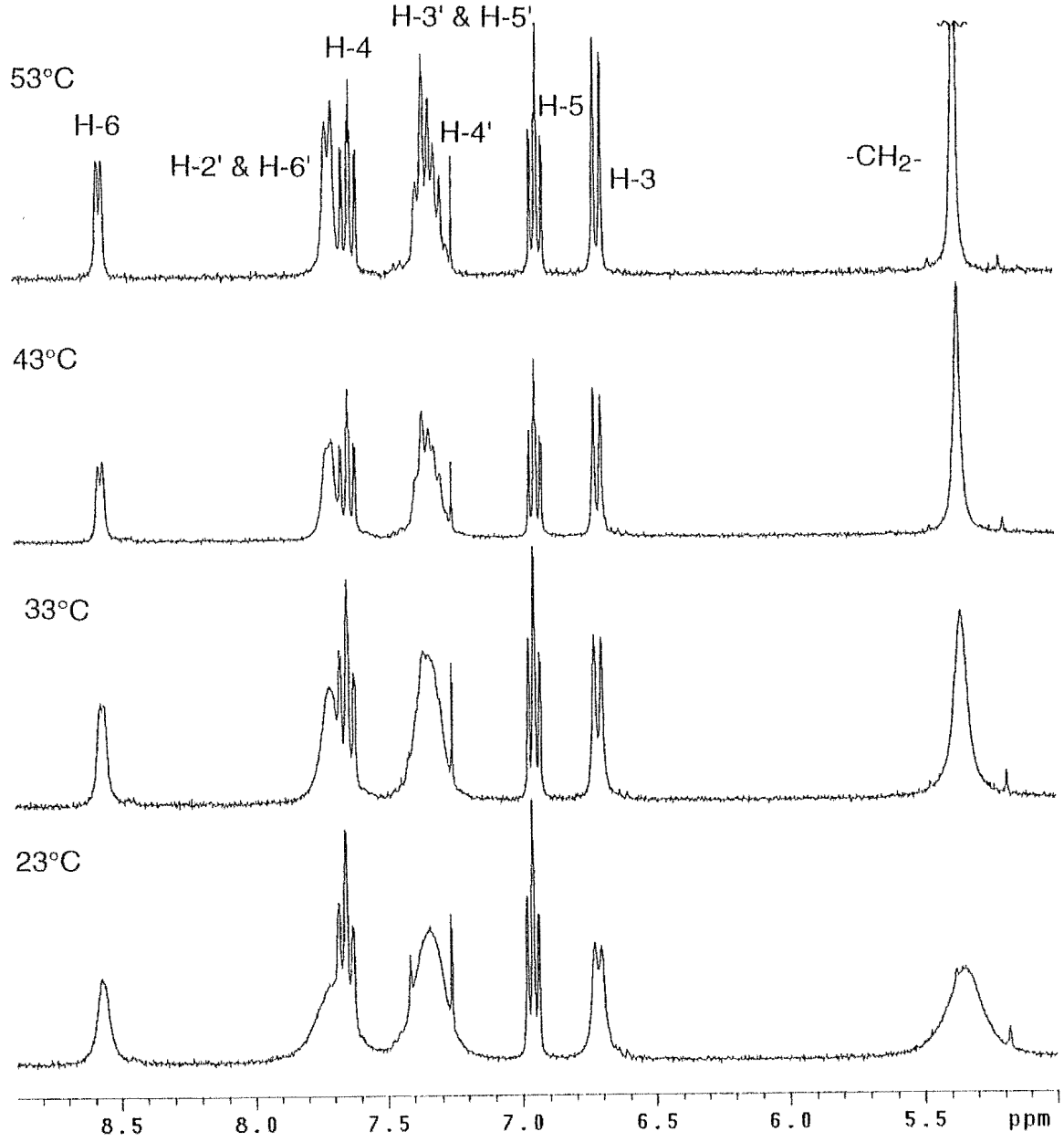
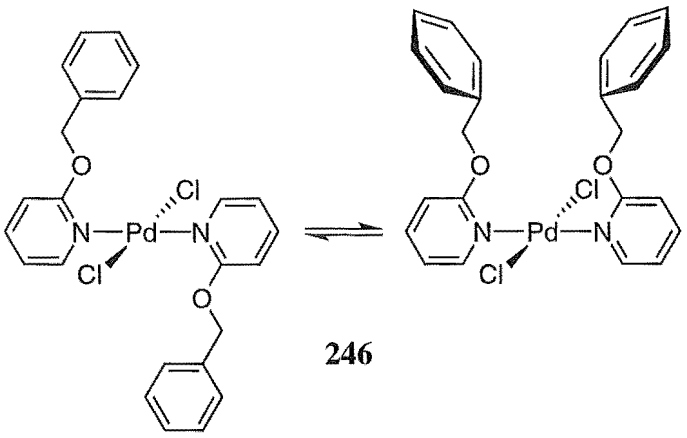


Figure 2.15 Variable temperature ^1H NMR spectra of **246**

Acquisition, at ambient temperature, of ^{1}H NMR data for the complex gave a spectrum (figure 2.15) in which only two triplets were resolved, all other resonances displaying significant broadening. Acquisition of spectra at increasing temperatures saw all of the resonances sharpen and take on the familiar coupling pattern of the ligand, confirming that the ligand was not cyclometallated. Subsequent homonuclear decoupling experiments permitted the assignment of all signals in the spectrum and the two resonances which are not broadened at the lower temperature were assigned to H-3 and H-4 of the pyridine ring.

The ^{13}C NMR spectrum was acquired only at ambient temperature because, given the low solubility of the complex, acquisition of a spectrum at higher temperature would necessitate a large number of transients with consequent risk of damage to the NMR probe. The ^{13}C NMR spectrum so recorded enabled the assignment of all signals, with those for the *ortho* carbons and for C-6 being the most broadened. Hence, the complex was fully characterised, the NMR data supporting the formulation of the complex as **246**.

The nature of the temperature dependent process which leads to the broadening of the NMR spectra is assumed to be interconversion between *syn* and *anti* rotamers as has been observed for a number of related *trans*-dichloropalladium coordination complexes described above (scheme 2.18).



246

ANTI ***SYN***

Scheme 2.18

Reaction of **242** with lithium tetrachloropalladate was carried out without stirring of the reaction mixture, as in the reaction of **241**. Again, no crystals were formed and the product was obtained as a yellow powder. Microanalysis, following recrystallisation by diffusion of petroleum ether into a chloroform solution of the product, gave the formulation $Pd(\mathbf{242})_2Cl_2$ (**247**), which again suggested the formation of a coordination complex, assumed to have *trans* stereochemistry.

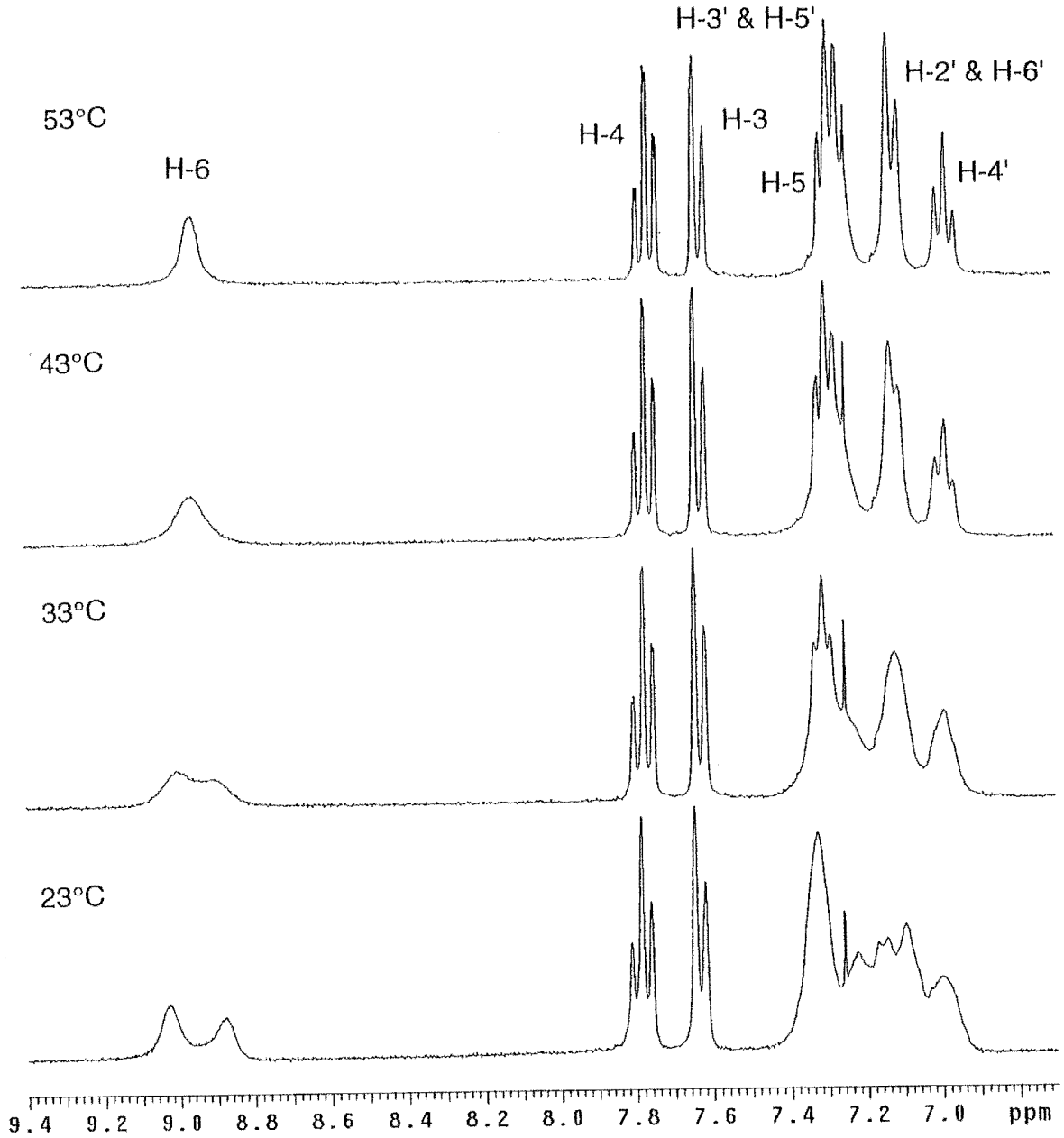
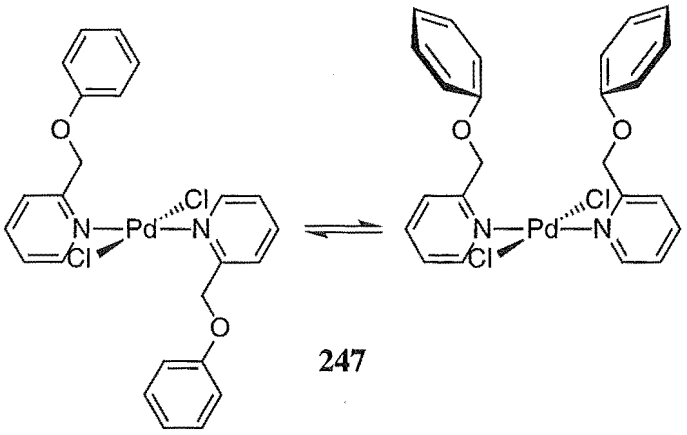


Figure 2.16 Variable temperature ^1H NMR spectra of **247**

As with the analogous complexes, **234** and **246**, the ^{1}H NMR spectrum of the above complex displays an interesting temperature effect (figure 2.16). At ambient temperature there are only two well-resolved signals in the spectrum, and these are assigned to the resonances for H-3 and H-4 on the pyridine rings. 1D-TOCSY experiments enabled the assignment of the resonances for H-5 and H-6 with these two signals appearing as a broad singlet and a broad doublet respectively. The resonances for the phenyl ring protons are all broad and overlap to such an extent that their assignment is not possible. Upon heating to 53°C all resonances sharpen appreciably and are able to be assigned with the *ortho*, *meta* and *para* protons appearing as the expected doublet, triplet and triplet respectively. The resonance for H-6 is not as well-resolved as might be expected at this temperature and it appears as a broad signal rather than a sharp doublet.

The ^{13}C NMR spectrum of **247** has only been acquired at ambient temperature because of low solubility. However, at this temperature the signals for C-6, *ortho* and methylene carbons are quite broad, the broadening of the latter of particular interest as this is not reflected in the NMR spectrum of the attached protons.

The nature of the temperature dependent process which leads to the broadening of the NMR spectra of **247** is assumed to be the same as that observed for **246**, namely interconversion of *syn* and *anti* rotamers which is relatively fast on the NMR timescale (scheme 2.19). It is noteworthy that in the variable temperature ^{1}H NMR spectra of **246** and **247**, the signal for the methylene protons is broadened in the spectrum of **246** but not in the spectrum of **247**. A possible explanation is that, in **246**, the methylene group is adjacent to the phenyl ring and, therefore, its magnetic environment is more influenced by the relative positions of the phenyl rings—that is, *syn* or *anti* —than is the environment of the corresponding methylene group in **247**, which has an oxygen atom between it and the phenyl ring.



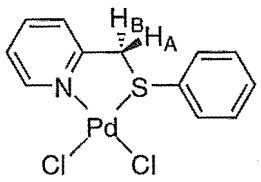
247

ANTI *SYN*

Scheme 2.19

Reaction of **243**, the thioether analogue of **241**, with lithium tetrachloropalladate gave the coordination complex, Pd(**243**)$_2$Cl$_2$ as a pale yellow powder in good yield. This complex is insoluble in common NMR solvents and was characterised, therefore, by IR spectroscopy and microanalysis.

As discussed above, **244** is the only ligand in this series for which there is any literature report of complexation reactions, the ligand coordinating to platinum(II) in a bidentate fashion.[159] Reaction of this ligand with lithium tetrachloropalladate gave the corresponding dichloropalladium(II) complex, Pd(**244**)Cl$_2$ (**248**) as analytically pure, orange microcrystals which are insoluble in chloroform but display good solubility in DMSO. The complex was fully characterised by FAB mass spectrometry and by IR and ^{1}H and ^{13}C NMR spectroscopy. The appearance of the geminal methylene protons as an AB quartet in the ^{1}H NMR spectrum further confirms the formation of a chelate ring containing the methylene bridge.



248

It is interesting to contrast the product obtained upon reaction of **242** with lithium tetrachloropalladate to that obtained upon reaction of the analogous thioether,

244. As discussed above, reaction of the ether gives a bis-ligand mononuclear dichloropalladium complex in which the ligands are coordinated solely through the pyridyl nitrogen. Reaction of the thioether, however, gives a mononuclear dichloro complex in which the ligand is coordinated in a bidentate fashion through the pyridyl nitrogen *and* the sulfur atom. This is consistent with the fact that palladium(II) is a 'soft' metal that shows a preference for bis-monodentate N-coordination over *N,O*-bidentate coordination, and *N,S*-bidentate coordination over bis-monodentate N-coordination, upon reaction—under the same conditions—with these structurally related ligands.

Having established that reaction with lithium tetrachloropalladate does not lead to cyclopalladation, with concomitant formation of a seven-membered palladacycle, the reactions of the four ligands with palladium acetate were investigated, as were the reactions with rhodium trichloride. Regardless of solvent or temperature, all attempts at direct cyclometallation of the ligands with these reagents were unsuccessful. Subsequent attempts at indirect cyclometallation *via ortho*-lithiated derivatives (*vide supra*) were also unsuccessful with unreacted ligand being recovered from the attempted lithiation reactions.

An alternative approach to the indirect cyclometallation of N-donor ligands is *via* the bis-ligand dichloro coordination complex. Abstraction of halogen atoms from these complexes creates coordinative unsaturation at the metal centre, increasing its electrophilicity and promoting subsequent attack on, and cleavage of, the *ortho*-carbon-hydrogen bond of the adjacent aryl ring.[172,173] Application of this method to primary benzylamines has facilitated the preparation of cyclo-palladated and -platinated complexes which are not accessible *via* direct cyclometallation reactions.[174,175]

Some preliminary investigations on this type of reaction had been performed on the N-coordinated 2-phenoxypyridine complex, **234**, but subsequent direct cyclopalladation of this ligand removed the impetus from these studies. Given the availability of both **246** and **247**, the seeming unreactivity of both ligands to direct

cyclometallation and the stated aim to prepare complexes with seven-membered metallocycles, their reactions with silver tetrafluoroborate were investigated. This silver salt was selected because tetrafluoroborate is a poorly coordinating anion and as such should, upon chloride abstraction from the complex, maximise the electrophilicity of the palladium centre.

Reaction of **246** with silver tetrafluoroborate[175] gave, upon filtration, a precipitate of silver chloride the weight of which corresponded to the removal of both chloro ligands from the palladium centre. Despite this initial success all subsequent attempts to isolate palladium complexes from the filtrate gave, at best, insoluble solids were could not be characterised.

Similar reaction of **247** also gave a precipitate of silver chloride corresponding to the removal of both chloro ligands. Exhaustive attempts to isolate palladium complexes from the reaction mixture, after addition of sodium bromide, gave a small quantity of well-formed orange needles suitable for single crystal X-ray structure determination.

The solving and refinement of a partial X-ray data set revealed that the crystals were not of the desired bromo-bridged cyclopalladated dimer, but of the coordination complex, *trans*-Pd(**242**)$_2$Br$_2$ (**249**) (figure 2.17). Of particular interest in the structure of this complex is the fact that the phenyl rings lie approximately coplanar with the coordinated pyridine rings, in contrast to the orthogonal arrangement observed for **234** (*vide supra*). Given that the relatively poor quality of the crystal used for the collection of this data set and that the complex was not cyclopalladated, further data were not collected and the structure was not further refined.

The reaction of **242** with potassium tetrabromopalladate in methanol was carried out for the purposes of comparing the product with the mixture of complexes obtained above. The reaction mixture was left to stand overnight without stirring in order to allow direct formation of a crystalline product. The product was obtained as fine yellow needles, the melting point, IR and ^{1}H NMR spectra of which were identical to

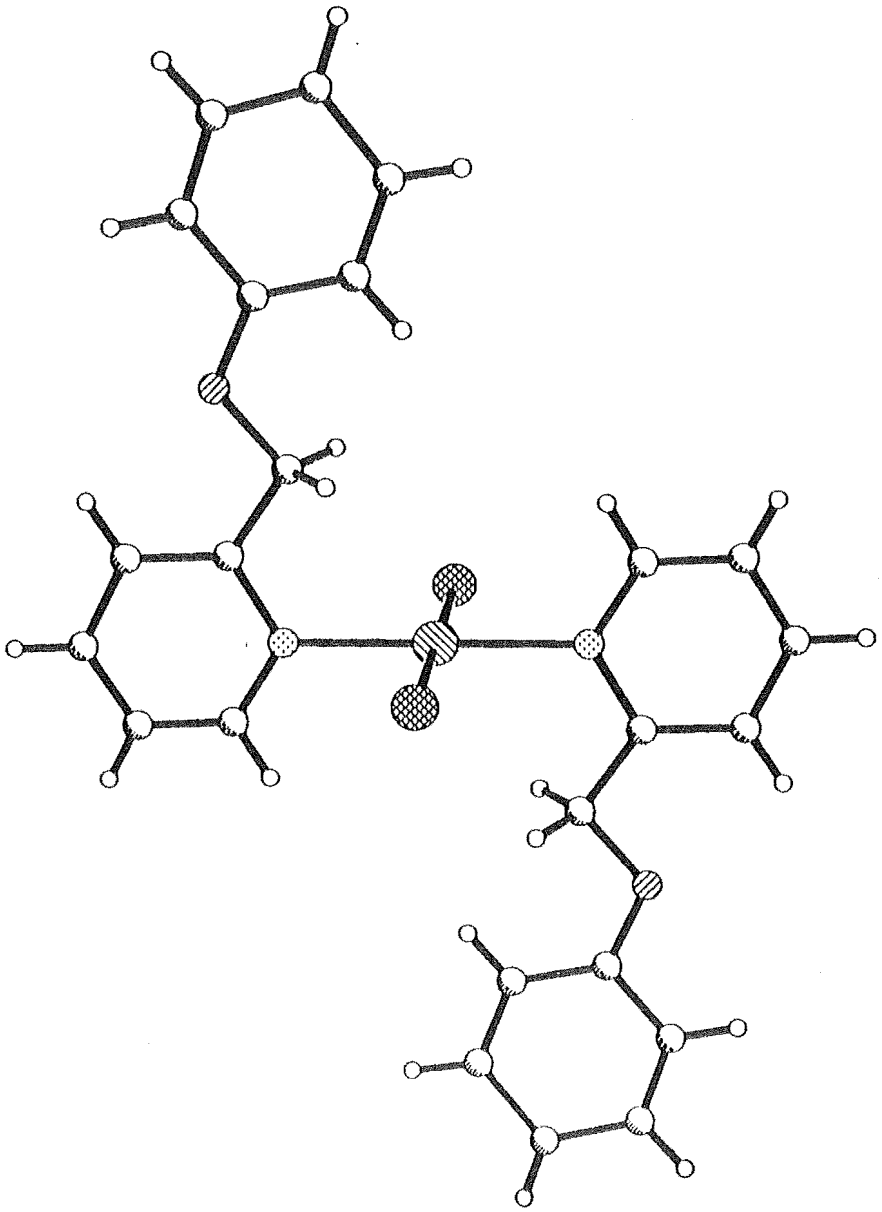


Figure 2.17 Perspective view of **249**

that of the orange needles obtained upon reaction of **247** with silver tetrafluoroborate. Examination of the ^{1}H NMR spectrum of the dibromopalladium complex, **249**, which is unchanged upon heating above ambient temperature, suggests that the complex forms as a mixture of *syn* and *anti* rotamers which are interconverting slowly, if at all, on the NMR timescale. This is in contrast to the dichloropalladium complex, **247**, which does show interconversion at ambient temperature, the difference in observed temperature dependence presumably due to the increased rotational barrier upon replacement of the chlorine atoms with the significantly larger bromine atoms.

2.5 CONCLUSION

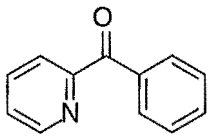
In summary, the preparations of several noteworthy complexes have been described. Of particular note is the coordinatively unsaturated rhodium complex, **204**. The preparation and characterisations of the cyclopalladated complexes, **237** and **239**, both of which incorporate a six-membered metallocycle have also been described. A number of the complexes exhibit temperature-dependent NMR spectra and an explanation for the molecular processes leading to this observation, based on common and changing structural elements in the complexes, has been proposed. All attempts to prepare greater than five-membered rhodacycles were unsuccessful, as were attempts to prepare seven-membered palladacycles from a series of four pyridine-containing ligands.

Chapter Three

Reactions of 2-Benzoylpyridine with Rhodium Trichloride

3.1 INTRODUCTION

The coordination chemistry of 2-benzoylpyridine (**301**) has been regularly studied in the past. This versatile ligand has been reported to coordinate in a variety of modes. In coordination complexes it can act as a monodentate ligand, with coordination by either the nitrogen[176-179] or oxygen atom;[180] as a *N,O*-bidentate coordinated ligand with a five-membered chelate ring;[176,181-185] or as a bridging *N,O*-coordinated ligand in binuclear complexes.[177]



301

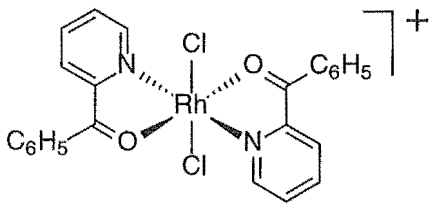
The reactions of **301** with palladium chloride[186] and palladium acetate[54,186,187] have been reported, the former giving rise to a coordination complex, Pd(**301**)$_2$Cl$_2$ and the latter to a cyclopalladated acetate-bridged dimer, [Pd(**301**-H)(OAc)]$_2$, in which **301** acts as a *N,C*-coordinated ligand and forms a six-membered metallocycle. Ligand exchange of this acetate-bridged dimer with lithium chloride gives the chloro-bridged analogue, [Pd(**301**-H)Cl]$_2$,[54,186] which has also been indirectly prepared from the ligand *via* a transmetallation reaction.[125] Reaction of the chloro-bridged dimer with thallium acetylacetonate[186] or sodium acetylacetonate[54] gives the corresponding mononuclear complex, Pd(**301**-H)(acac), which has been fully characterised by ^{1}H and ^{13}C NMR spectroscopy.[54]

The reaction of **301** with rhodium(III) trichloride under mild conditions has been previously reported.[188,189] This reaction has been re-examined and attempts made to induce cyclometallation reactions under more vigorous reaction conditions. This chapter reports the results of these attempts, together with the single crystal X-ray crystal structures of three rhodium complexes of 2-benzoylpyridine, in two of which it acts as an N-O chelating ligand and in the other as a cyclorhodated *N,C*-bidentate ligand.

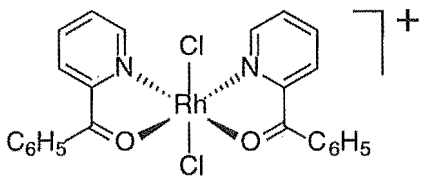
3.2 REACTIONS OF 2-BENZOYLPYRIDINE WITH RHODIUM(III) TRICHLORIDE.

Although some ligands readily undergo cyclorhodation with rhodium trichloride in refluxing ethanol, it has previously been reported that reaction of **301** under these conditions does not effect cyclometallation.[188] Osborne and McWhinnie described a series of octahedral rhodium(III) complexes of **301**, to which they tentatively assigned structures on the basis of IR spectroscopic data.[188] These reactions have been re-examined and ^{1}H and ^{13}C NMR spectroscopy and single crystal X-ray diffraction studies used to assign the structures more definitively.

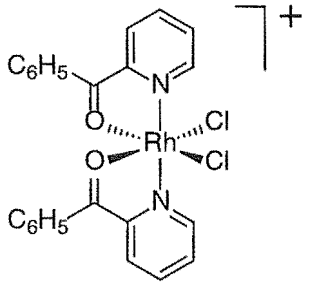
Reaction of **301** with rhodium(III) trichloride trihydrate and sodium perchlorate in refluxing aqueous ethanol gives, as previously reported, a yellow salt that was assigned[188] the centrosymmetric structure **302**. In accord with this proposed structure, the ^{1}H NMR spectrum (table 3.1, p.89) shows that the two coordinated ligands are symmetrically equivalent. However, four possible structures, **302-305** (figure 3.1), would fulfil this condition, and so it was necessary to obtain crystals of the complex for a single crystal X-ray structure determination. Recrystallisation from acetonitrile/methanol furnished suitable crystals as yellow blocks.



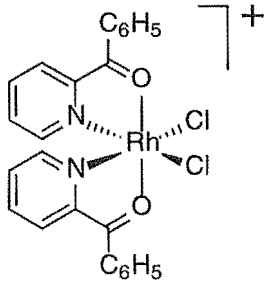
302



303



304



305

Figure 3.1

Crystal Structure of $Rh(\mathbf{301})_2Cl_2.ClO_4$

The rhodium complex, $Rh(\mathbf{301})_2Cl_2.ClO_4$, crystallises in the monoclinic space group C2/c, the asymmetric unit of which comprises half a molecule of the octahedral cation, which lies on a crystallographic centre of inversion, and half a perchlorate anion, which lies on a two-fold rotation axis (figure 3.2).

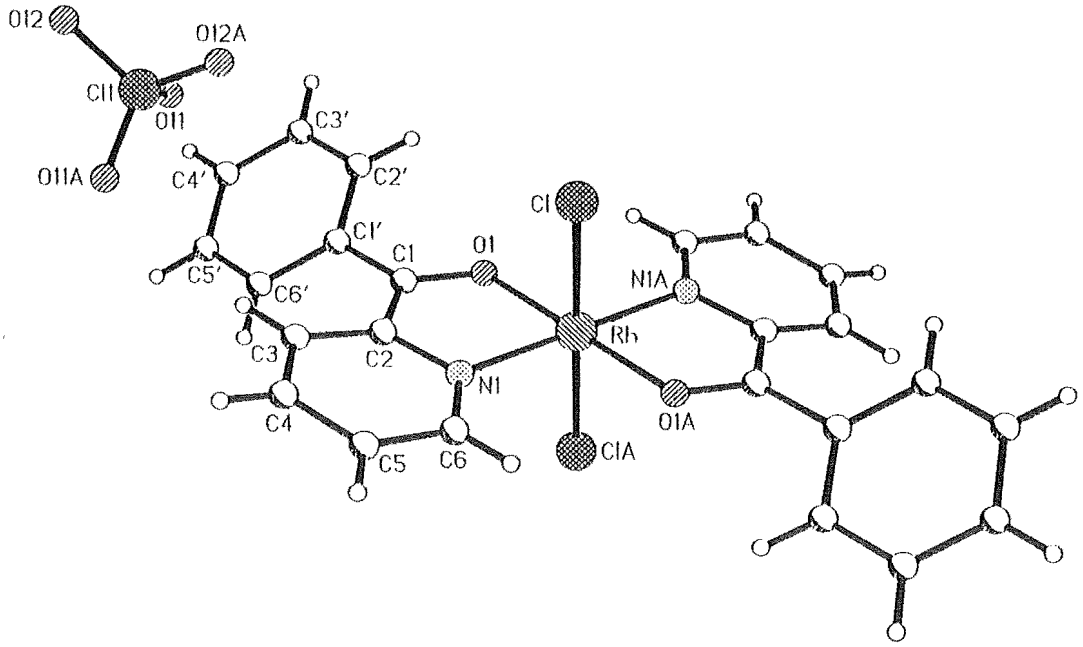


Figure 3.2 Perspective view and atom labelling of $Rh(\mathbf{301})_2Cl_2.ClO_4$. Selected bond lengths (Å) and angles (°): Rh-N1 2.019(2), Rh-O1 2.009(2), Rh-Cl 2.3212(7); N1-Rh-O1 80.25(8), N1-Rh-Cl 88.17(7), C1'-C1-C2 124.0(2).

This single crystal X-ray analysis thus confirms the structure of the yellow complex as being the centrosymmetric isomer **302** previously proposed.[188] The geometry about the rhodium atom is octahedral, in contrast to some of the six-coordinate copper complexes of **301,** which contain relatively long copper-oxygen bonds.[181-185] The 2-benzoylpyridine ligand is coordinated in a *N,O*-bidentate mode and has similar bonding geometry to that previously reported for a number of copper complexes of **301**.[181-185] The five-membered chelate ring deviates slightly from planarity

(Rh1-N1-C2-C1 torsional angle = 10.9 °) and is inclined to the phenyl ring mean plane at an angle of 37.0 °. There are no unusually short intermolecular contacts.

Upon warming in water, the yellow complex **302** has been reported to undergo rearrangement to an orange isomer, that was assigned structure **303** on the basis of infrared data.[188] This reaction is found to be somewhat variable, in that it also produces a second product that is discussed below. The orange isomer is more conveniently prepared in quantitative yield (by ^{1}H NMR spectroscopy), from an acetonitrile solution of **302** left to stand at room temperature for 24 hours. The ^{1}H and ^{13}C NMR spectra of the orange isomer (tables 3.1 and 3.2, p.89 and 90) also show that the two coordinated ligands are in identical environments. However, this would be consistent with not only the C_{2v} isomer **303**, but also the two C_2 isomers **304** and **305** and, therefore, further investigation of the structure of this complex was required. Diffusion of ether vapour into an acetonitrile solution of this orange complex produces very thin yellow plates, which were used for a single crystal X-ray crystal structure determination.

Crystal Structure of rearranged Rh(**301**)$_2$Cl$_2$.ClO$_4$

The rearranged rhodium complex, Rh(**301**)$_2$Cl$_2$.ClO$_4$, crystallises in the monoclinic space group C2/c, the asymmetric unit of which contains the octahedral cation, a disordered perchlorate anion and two molecules of acetonitrile (figure 3.3).

This single crystal X-ray structure determination reveals that this isomer has, in fact, the C_2 structure **304**, with *cis*-chlorides and *trans*-nitrogens, rather than the previously proposed *trans*-dichloride structure **303**. The potential C_2 symmetry of the cation is destroyed in the solid state by torsion angle differences in the orientations of the phenyl rings. The bonding geometry about the rhodium atom and within the 2-benzoylpyridine ligands is similar to that in the complex **302**. Again, there are no unusually short non-bonded interactions.

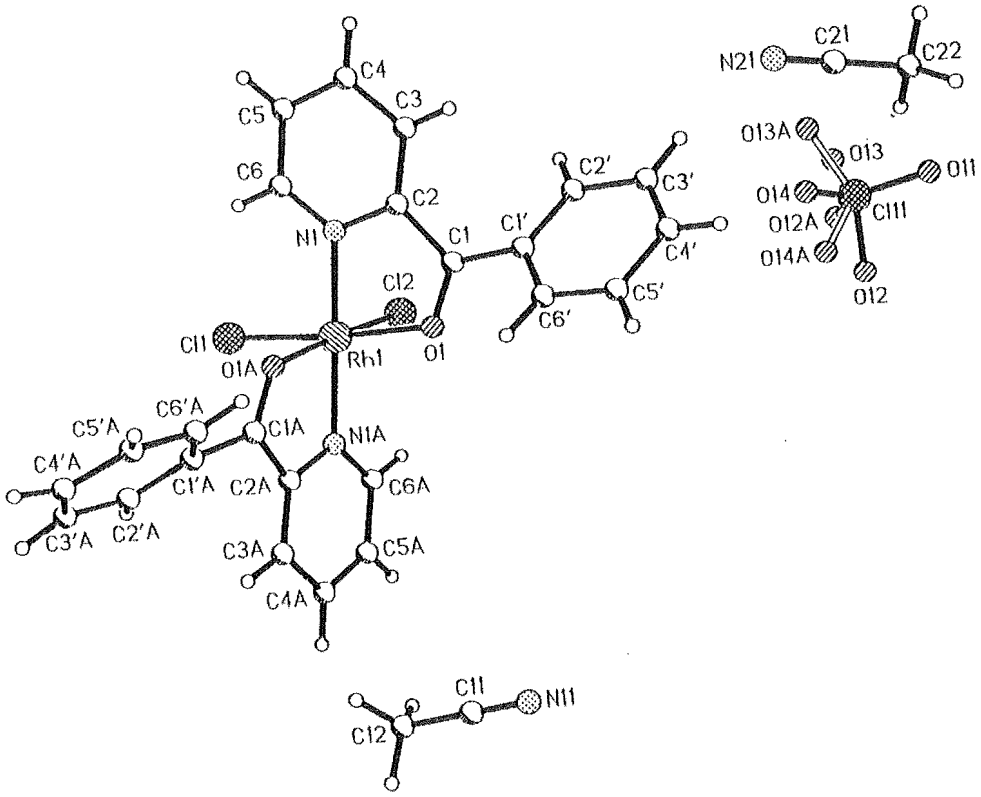


Figure 3.3 Perspective view and atom labelling of rearranged $Rh(\mathbf{301})_2Cl_2.ClO_4$. Selected bond lengths (Å) and angles (°): Rh-N1 2.009(8), Rh-N1A 2.013(8), Rh-O1 2.051(8), Rh-O1A 2.051(8), Rh-Cl1 2.290(4), Rh-Cl2 2.307(4); N1-Rh-N1A 174.2(4), N1-Rh-O 79.5(3), N1A-Rh-O1A 79.9(3), Cl1-Rh-Cl2 91.7(1).

As described above, **302** undergoes rearrangement to **304** on warming in water. This reaction also produces varying amounts of a red compound, the yield of which increases with time. Recrystallisation of this mixture from methanol/acetonitrile afforded a pure sample of this compound **306**, as very fine needles, which were unsuitable for single crystal X-ray crystallographic structure determination. The ^1H NMR spectrum of these needles (table 3.1, p.89) is considerably more complex than that of **302** or **304** and shows the presence of two **301** ligands in chemically different environments. Complete assignment of this spectrum was achieved by means of a series of one- and two-dimensional techniques. Specifically, the individual spin systems were located by

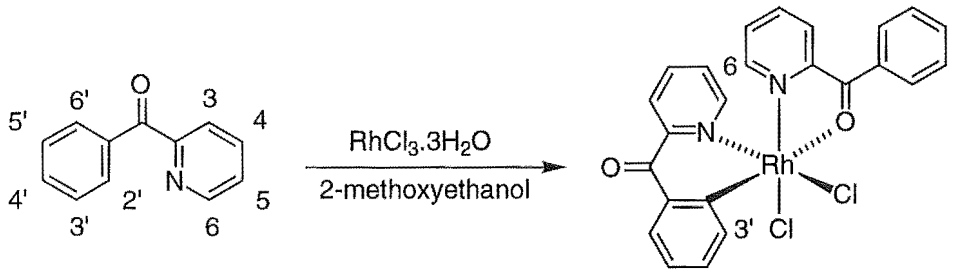
means of 1D-TOCSY and COSY techniques and the two rings within each ligand were paired up by difference NOE spectroscopy on the basis of an NOE enhancement of the *ortho* protons of the phenyl ring on irradiation of the signal for the H-3 proton of the pyridine ring.

Comparison of the chemical shifts of the two ligands in **306** with the spectra of **302** and **304** (table 3.1) clearly shows that one of the ligands is coordinated in a *N,O*-bidentate mode and the other in a monodentate mode. The ^{1}H NMR spectrum, IR spectra, microanalysis and the fact that this compound is a non-electrolyte, are in agreement with the structure proposed by the previous workers[188] who suggested that this compound, **306**, is an octahedral rhodium complex containing two chloride ligands, one hydroxy ligand, and two **301** ligands one of which is *N,O*-bidentate and the other *O*-monodentate. The exact stereochemistry of this compound remains unknown.

In acetonitrile solution, this compound undergoes further rearrangement over a period of 6 days at room temperature to a new complex **307** which also has one *N,O*-bidentate and one monodentate ligand. The ^{1}H and ^{13}C NMR spectra of **307** (tables 3.1 and 3.2) were again fully assigned using techniques similar to those described above. Again, the exact structure of this compound remains unknown; it does, however, display an interesting exchange phenomenon. Although the two benzoylpyridine ligands were not observed to exchange on the NMR timescale, they were shown to undergo slow exchange by magnetisation transfer experiments. In particular, irradiation of the pyridine H-3 proton (at 7.08 ppm) of the monodentate ligand resulted in transfer of magnetisation to the signal (at 8.57 ppm) for H-3 of the bidentate ligand. This exchange process presumably occurs by dissociation of the bidentate ligand to a five-coordinate intermediate, followed by chelation of the ligand which had originally been monodentate: a degenerate exchange process.

The original aim of the investigation of the reactions of rhodium(III) with **301** was to effect cyclorhodation of the ligand. To this end the reaction with rhodium trichloride trihydrate under more vigorous reaction conditions was investigated. Reaction of rhodium trichloride trihydrate with two equivalents of **301** in refluxing

2-methoxyethanol gave a complex, formulated as Rh(**301**-H)(**301**)Cl_2 (**308**), in high yield (Scheme 3.1). This complex is soluble in chloroform and was shown by NMR, IR spectroscopy and microanalysis to be a mononuclear rhodium complex containing two chloride ligands and two **301** ligands in different modes of coordination, one of which is cyclometallated. The existence of the cyclorhodated ligand in the complex was revealed in the ^1H NMR spectrum by the conversion of a five proton phenyl-ring spin system into a four proton system resonating between 7.4 and 8.0 ppm and located and assigned by a 1D-TOCSY experiment. The full assignment of the ^1H and ^{13}C NMR spectra of **308** (tables 3.1 and 3.2) were made by methods similar to those described above.



301 **308**

Scheme 3.1

A mononuclear octahedral complex containing two identical monodentate ligands and two different chelating ligands can exist as six possible diastereoisomers. Of the six possible structures for the above compound the structure shown, **308**, was deduced to be the most probable on the following basis: (i) a comparison of the NMR chemical shifts with those of other cyclorhodated compounds;[186,187] (ii) the fact that cyclorhodation of nitrogen containing ligands usually produces complexes with *cis*-chlorides;[186,187] (iii) a *trans*-dichloride isomer with a cyclometallated ligand would be highly sterically hindered; and (iv) most importantly, the observation of a significant NOE enhancement of the signal for H-3' (at 7.89 ppm) of the metallated benzene ring on irradiation of the pyridine H-6 proton (at 8.99 ppm) of the non-cyclometallated ligand, which requires these two rings to be mutually *cis*.

Osborne and McWhinnie reported that the red complex, **306**, could be formed from the yellow complex, **302**, or the orange complex, **304**, by warming in water (*vide supra*). Refluxing this red complex in 75% aqueous ethanol gave a yellow product, soluble in chloroform, which they formulated as Rh(**301**)$_2$Cl$_3$.[188] This complex contains two **301** ligands and it was reported that one is coordinated in a bidentate fashion through the nitrogen and oxygen atoms, whilst the other is monodentate *N*-coordinate.[188] This reaction sequence was repeated and, indeed, found to give a yellow complex which was found to be soluble in chloroform. However, rather than having the structure described above, this complex was found by IR and ^{1}H NMR spectroscopy to be the yellow complex, **308**, the second ligand being cyclorhodated rather than *N*-monodentate. Examination of the microanalysis data in the original report[188]—in which there is no chlorine analysis—suggests that the authors had, in fact, prepared Rh(**301**-H)(**301**)Cl$_2$.2^1/$_2$H$_2$O, rather than Rh(**301**)$_2$Cl$_3$.

In order to confirm unambiguously the stereochemistry of **308**, attempts were made to recrystallise a sample of the complex for a single crystal X-ray structure determination. A variety of solvents and solvent mixtures were used but these attempts gave, at best, fine yellow needles unsuitable for crystallography. However, an attempted recrystallisation by diffusion of pentane into a DMSO/chloroform solution of the complex produced yellow crystals suitable for X-ray analysis. The X-ray crystal structure and elemental analysis of these crystals showed that they were not of the original complex but of a solvolysis derivative.

Crystal Structure of Rh(**301**-H)(DMSO)$_2$Cl$_2$

The rhodium complex, Rh(**301**-H)(DMSO)$_2$Cl$_2$ (**309**), crystallises in the monoclinic space group P2$_1$/n, the asymmetric unit of which is comprised of a rhodium atom coordinated to a single cyclometallated ligand, two *cis*-chloride ligands and two DMSO ligands, one coordinated through sulfur and the second through oxygen, and a disordered solvate molecule (figure 3.4). This solvate molecule was initially thought to be a highly disordered chloroform molecule, but attempted refinement as such was unsuccessful. After many trial attempts at refinement it became apparent that the solvate

site was occupied by both a chloroform and a DMSO molecule, with equal (half) occupancies. This is the solvent combination from which the crystals had deposited. In support of this interpretation, elemental analysis of these crystals indicated the presence of half a molecule of DMSO as solvate, the chloroform having been lost on drying.

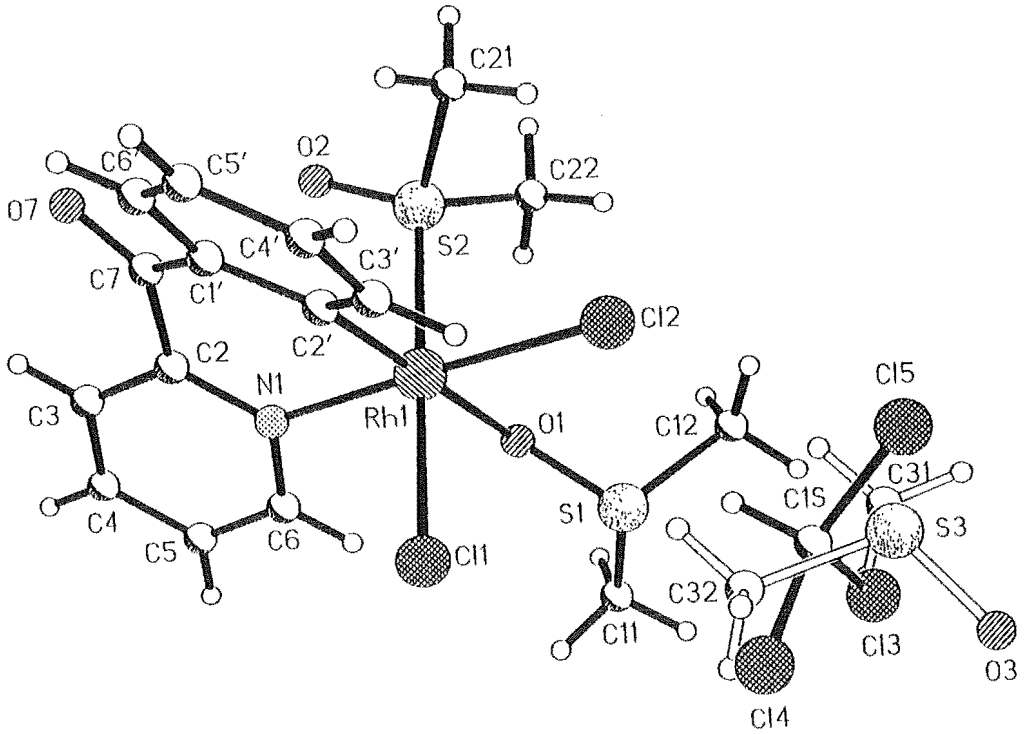
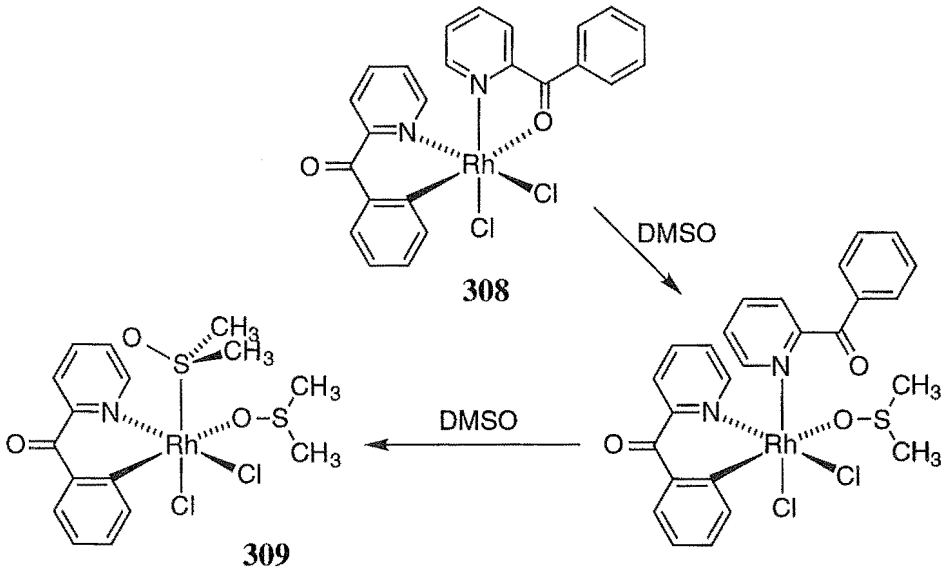


Figure 3.4 Perspective view and atom labelling of **309**. Selected bond lengths (Å) and angles (°): Rh1-C2' 2.005(5), Rh1-N1 2.051(4), Rh1-O1 2.234(3), Rh1-S2 2.227(1), Rh1-Cl1 2.355(1), Rh1-Cl2 2.346(1); N1-Rh1-C2' 89.6(2), Cl1-Rh-Cl2 92.11(5), S2-Rh1-O1 90.5(1), C2-C7-C1' 121.3(5).

The crystal structure determination unambiguously demonstrates that the ligand has undergone cyclometallation. This results in a six-membered chelate ring which exists in a boat conformation. It is well known that cyclometallations which produce six-membered metallocycles are more difficult to induce than those that produce five-membered rings (*vide supra*). The presence of varying numbers of differently coordinated DMSO ligands in a single complex has been reported previously for crystal structures of ruthenium(II),[190-193] ruthenium(III),[194] palladium(II),[195,196] platinum(II)[197] and rhodium(III)[198,199] complexes with monodentate ancillary ligands.

Structure **309** is the first single crystal X-ray structure to contain differently coordinated DMSO ligands together with a chelating ligand.

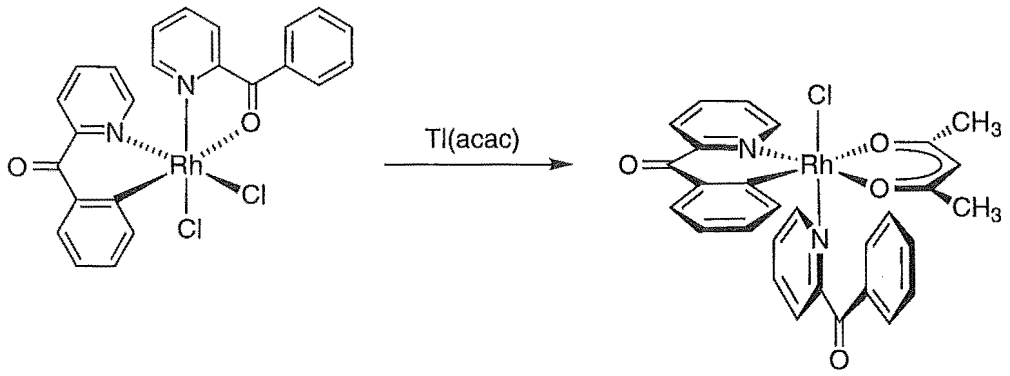
When coordinated through sulfur, DMSO is a weak π-acceptor ligand and when coordinated through oxygen it is a strong σ-donor.[193] This leads to a rationalisation for the formation of this novel complex **309** from **308** (scheme 3.2), and provides further support for the structure of **308**. Given the strong *trans*-effect of the metallated carbon donor, it is likely that the rhodium-oxygen bond is the weakest bond to rhodium in the complex **308**, and hence the most susceptible to substitution by DMSO. The metallated phenyl ring is a weak π-acceptor and a strong σ-donor. The DMSO coordinating *trans* to this ring is, therefore, unlikely to coordinate through sulfur, as this would lead to competition for electron density in dπ-donor orbitals on the Rh centre;[193] thus coordination through oxygen occurs for this DMSO molecule. Cleavage of the rhodium-oxygen bond in **308** converts the previously bidentate 2-benzoylpyridine ligand into a monodentate ligand coordinated through the pyridyl nitrogen. This results in a loss of stabilisation due to the chelate effect, which means that this ligand is prone to substitution by a second DMSO molecule. This DMSO ligand coordinates through sulfur due to the availability of electron density in dπ-donor orbitals on the Rh atom which results from the pπ-donor chloride ligand *trans* to it.



308 **309**

Scheme 3.2

The final reaction in this series to be investigated was the reaction of **308** with thallium acetylacetonate in dichloromethane. The reaction mixture was stirred for five days after which it was filtered and ether vapour diffused into the filtrate. This gave a small quantity of well-formed yellow crystals which were, unfortunately, not suitable for a single crystal X-ray structure determination. This complex is soluble in chloroform and acquisition of ^{1}H and ^{13}C NMR spectra in $CDCl_3$ (tables 3.1 and 3.2) revealed that, as expected, the cyclorhodated Rh(**301**-H) moiety had remained intact. The complex was also shown to contain, in addition to an acac ligand, another 2-benzoylpyridine ligand in which the phenyl ring, as before, was not metallated. Consideration of the chemical shifts of the observed resonances due to this ligand, suggests that this ligand is not coordinated in a *N,O*-bidentate fashion, as in **308**, but coordinated in a monodentate mode through the pyridyl nitrogen. An NOE difference experiment gave, upon irradiation of the signal due to H-3' on the cyclorhodated phenyl ring, enhancement of the signal due to the *ortho* protons of the free phenyl ring. The formulation of the complex, is therefore, most likely to be Rh(**301**-H)(**301**)Cl(acac) (**310**), with the structure of the complex as shown (scheme 3.3).



308 **310**

Scheme 3.3

In summary, it has been shown that, in contrast to the reactions in refluxing ethanol, 2-benzoylpyridine can be made to undergo cyclorhodation under forcing conditions. The reaction product is not, however, the normal chloro-bridged dimer with two cyclometallated ligands on each rhodium, but a novel complex, **308**, containing the ligand in two different bidentate modes of coordination (*N,C* and *N,O*). Whilst crystals

of this complex suitable for single crystal X-ray structure determination could not be obtained, the preparation and structure determination of a solvolysis product has provided indirect support for the structure of the novel complex.

Table 3.1 ^{1}H NMR chemical shifts for **301** and its rhodium complexes

Cmpd	Solvent	Mode[a]	*H-3*	*H-4*	*H-5*	*H-6*	*ortho*	*meta*	*para*
301	CD_3CN		**8.05**	**8.05**	**7.64**	**8.74**	**8.06**	**7.57**	**7.70**
302	CD_3CN	*N,O*	8.83	8.65	8.43	9.93	8.29	7.87	8.08
304	CD_3CN	*N,O*	8.75	8.62	8.39	9.93	8.04	7.75	7.96
306	CD_3CN	*N,O*	8.64	8.44	8.17	9.54	8.17	7.81	8.00
		N	6.99	7.95	7.67	9.52	7.84	7.43	7.43
307	CD_3CN	*N,O*	8.57	8.44	8.22	9.83	8.00	7.75	7.94
		N	7.08	7.97	7.68	9.74	7.51	7.29	7.29
301	$CDCl_3$		**8.05**	**7.92**	**7.50**	**8.74**	**8.07**	**7.50**	**7.60**
308	$CDCl_3$	*N,O*	8.19	8.08	7.73	8.99	8.09	7.69	7.82
		N,C	8.33	8.05	7.60	9.70	7.99[b]	7.30[c] 7.89[d]	7.45[e]
310	$CDCl_3$	*N*	7.08	7.71	7.12	7.78	7.92	7.39	7.32
		N,C	8.14	7.94	7.43	9.22	7.93[b]	7.18[c] 6.92[d]	7.14[e]
301	DMSO		**8.09**	**8.17**	**7.77**	**8.82**	**8.06**	**7.64**	**7.77**
308	DMSO	*N,O*	8.53	8.46	8.16	8.88	8.26	7.88	8.03
		N,C	8.35	8.42	8.03	9.63	7.87[b]	7.40[c] 7.90[d]	7.57[e]

[a] Coordination mode/s of the 2-benzoylpyridine ligands in each complex

[b] H-6' [c] H-5' [d] H-3' [e] H-4'

Table 3.2 ^{13}C NMR chemical shifts for **301** and its rhodium complexes

Cmpd	Solvent	Mode[a]	*C-3*	*C-4*	*C-5*	*C-6*	*ortho*	*meta*	*para*
301	CD_3CN		125.1	138.3	127.4	149.5	131.7	129.0	133.8
304	CD_3CN	*N,O*	137.1	142.8	134.6	155.6	132.2	130.6	137.8
307	CD_3CN	*N,O*	135.7	141.2	133.3	154.8	131.3	130.5	136.7
		N	125.2	140.4	125.7	151.2	127.4	128.7	128.6
301	$CDCl_3$		124.6	137.0	126.1	148.5	130.9	128.1	132.9
310	$CDCl_3$	*N*	123.7	138.2	123.1	148.2	127.2	128.1	127.7
		N,C	125.4	138.3	126.0	152.3	129.5[b]	123.6[c] 136.5[d]	130.2[e]
301	DMSO		124.3	137.8	126.9	148.7	130.7	128.4	133.2
308	DMSO	*N,O*	133.6	140.2	130.8	155.3	130.7	129.6	135.1
		N,C	125.9	140.2	127.5	153.7	128.0[b]	124.1[c] 139.5[d]	131.1[e]

[a] Coordination mode/s of the 2-benzoylpyridine ligands in each complex

[b] C-6' [c] C-5' [d] C-3' [e] C-4'

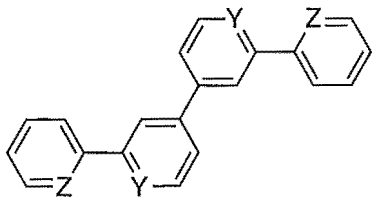
Chapter Four

Ligands Containing Two Cyclometallation Sites

4.1 INTRODUCTION

This chapter describes the preparations and reactions of a number of ligands which are potentially capable of giving doubly cyclometallated products. The ligands are divided into three groups based on structural similarity. Included is an investigation of the bromination of 2-phenylpyridine, carried out with a view to preparing precursors for two of the ligands herein described. Two of the ligands discussed have been previously cyclopalladated and the reactions of these with rhodium trichloride are described. The remaining ligands have all been reacted with lithium tetrachloropalladate and palladium acetate under a variety of conditions and the products characterised. One single crystal X-ray structure determination, which represents the first example of its kind, is also described.

4.2 QUATERPYRIDINE ANALOGUES

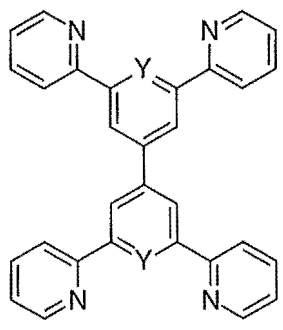


401 Y=N, Z=N
402 Y=N, Z=CH
403 Y=CH, Z=N

The preparations of the bis-chelating ligand 2,2':4',4":2",2"'-quaterpyridine (**401**) and its binuclear complex with bis(bipy)ruthenium(II) have recently been reported.[200] The complex showed a metal-metal interaction, the weakness of which was attributed to free rotation about the 4'-4" bond which disrupts the overlap of the π systems of the two 'bipy' subunits.[200] Given that the anion of 2-phenylpyridine (**201**) is the cyclometallated isoelectronic analogue of the well-studied chelating ligand, bipy, the possibility of preparing bis-cyclometallated analogues of the binuclear complexes of **401** with ligands that contained two symmetrically coupled **201** subunits, seemed worthy of investigation. The two ligands in question, 2,2'-diphenyl-4,4'-bipyridine (**402**) and 3,3'-di(2-pyridyl)biphenyl (**403**) have not previously been cyclometallated; indeed a search of Chemical Abstracts revealed that **402** has only been isolated as a

minor by-product in the preparation of **201**, by the reaction of phenylmagnesium bromide with pyridine 1-oxide in anhydrous benzene[201] and in the same reaction with THF as solvent,[202] while the preparation of **403** has not previously been reported.

A similar pair of ligands, binucleating analogues of 2,2':6',2''-terpyridine (terpy), have been prepared and their biruthenium(II) complexes studied. The biruthenium(II)(terpy) complex of the bis-chelating ligand 6',6''-di(2-pyridyl)-2,2':4',4'':2'',2'''-quaterpyridine (**404**) shows no electronic interaction between the two ruthenium centres[203] (with substitution of the ancillary terpy ligand in the 4' position having no effect on the lack of interaction[204]), whilst a biruthenium(II) complex of the bis-cyclometallated ligand 3,3',5,5'-tetra(2-pyridyl)biphenyl (**405**) shows strong electronic interaction between the two ruthenium centres.[205,206] Initially this was thought to be due to the fact that the ruthenium centres in the latter complex are connected by a 4,4'-biphenyl dianion bridge, with a torsion angle, in the solid state, about the central C-C bond of the bridging ligand of 22.2(7)°[205], whilst in the former the two metal ions are connected through a 4,4'-bipyridine bridge with the two central rings of the bridging ligand assumed to be perpendicular to one another in solution, thereby relieving steric interaction but preventing conjugation and π system overlap between the two 'terpy' subunits.[203] Given this information it was felt that the binuclear complexes of **402** and **403** could be expected to have different electrochemical properties, as in such complexes of **402** the two metal centres are connected by a 4,4'-bipyridine bridge, whilst in complexes of **403** the metal ions are connected by a 4,4'-biphenyl dianion bridge.



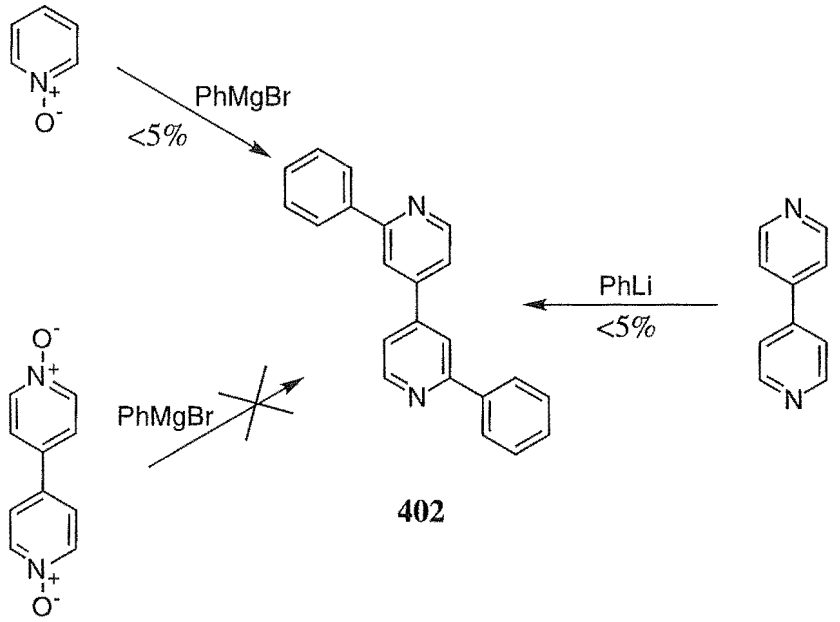
404 Y=N
405 Y=CH

Subsequently, however, the biruthenium(II)(6-phenyl-2,2'-bipyridine) complex of **404** was prepared and its metal-metal interaction measured. In this complex the two ruthenium centres are strongly coupled despite their being connected by a 4,4'-bipyridine bridge and, as a result of this, the strong electronic coupling between the two ruthenium centres in this complex and the biruthenium(II) complex of **405** is now attributed to the presence of two N_5C donor sets about the ruthenium centres.[207] Neither of the biruthenium(II) complexes of **404** have been characterised crystallographically and, therefore, the torsion angle between the two central rings of the bridging ligand for these two complexes, and the extent to which any differences in the electronic coupling between the metal centres could be accounted for by such differences and their effect on π system overlap between the two 'terpy' subunits, is not known.

Despite the differences in metal-metal interactions between the biruthenium complexes of the bis-chelating ligand, **404**, and the bis-cyclometallated ligand, **405**, being accounted for by the nature of the coordination sphere about the ruthenium ions, a comparison of similar complexes of **402** and **403** would provide further evidence to clarify this issue. In such complexes the only variable would be the positions of the nitrogen and carbon donors, relative to the bridging subunit, in the donor set of the bis-cyclometallated ligand. In the previous studies the position of the carbon donor varies between the bridging bis-cyclometallated **405** ligand and the spectator 6-phenyl-2,2'-bipyridine ligand for the analogous complex of **404**.

The synthesis of **402** has been investigated in earlier research with three approaches to the synthesis being employed with varying degrees of success (scheme 4.1).[208] Firstly the previously reported preparation of this compound[202] was repeated to give a poor yield (<5% of the crude reaction product, as estimated by ^{1}H NMR) of **402** which was not isolated. Secondly, phenylmagnesium bromide was reacted with 4,4'-bipyridine-1,1'-dioxide. However, despite obviating the need for pyridine coupling in the reaction mechanism, this reaction gave none of the desired product. Reaction of 4,4-bipyridine with phenyllithium, a reaction analogous to that used to prepare **201**

(*vide infra*), gave a complex mixture of products which was subjected to radial chromatography to give both 2-phenyl-4,4'-bipyridine and **402** in low yield.



402

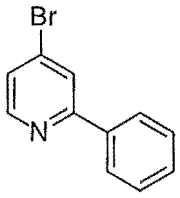
Scheme 4.1

Given the failure of these reactions to produce synthetically useful quantities of **402**, it was felt that the best approach to the synthesis of both **402** and **403** was by a fourth approach: the nickel(0)-catalysed coupling of appropriately halogenated 2-phenylpyridine precursors. This strategy is analogous to that used in the preparation of **401**[200] and, indeed, many other polyazine,[203,204,207] biheterocyclic,[209-213] and biaryl compounds.[210,211,214]

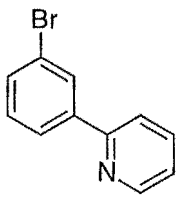
Utilisation of this procedure required the preparation of the halogenated precursors, namely 4-halo-2-phenylpyridine and 2-(3-halophenyl)pyridine. It has been shown that for nickel(0)-catalysed coupling reactions aryl bromides react faster and give higher yields of biaryls and bipyridines than do the corresponding aryl chlorides,[211] therefore the initial synthetic targets were 4-bromo-2-phenylpyridine (**406**) and 2-(3-bromophenyl)pyridine (**407**).

The bromopyridine **406** has previously been prepared by aromatisation of the dihydropyridine obtained from the reaction of 4-bromopyridine with phenylmagnesium chloride.[215] The bromobenzene **407** has previously been prepared by the treatment of diazotised 3-bromoaniline with pyridine to give the three isomeric

(3-bromophenyl)pyridines, which were then separated.[216,217] Given that none of the above methods gave either of the required compounds in greater than 50% yield, it was decided to investigate the possibility of preparing them by direct bromination of **201**. An extensive literature search revealed that no attempts to directly brominate **201** have been reported.



406



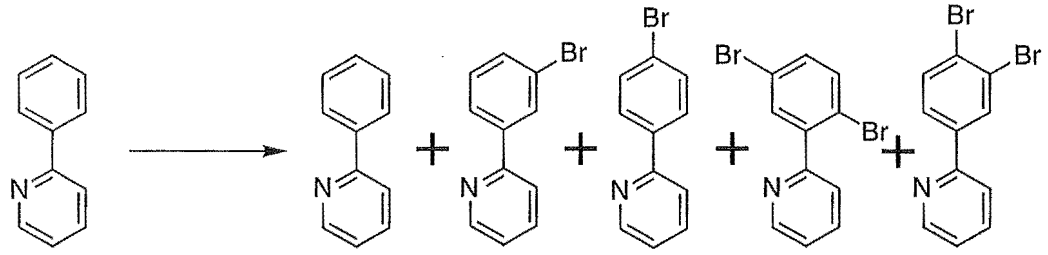
407

Given that bromination is an electrophilic substitution reaction, it would be expected that such a reaction of **201** would lead to bromination of the phenyl ring, rather than the pyridine ring, as the electron-withdrawing inductive effect of the electronegative nitrogen atom leads to low reactivity of pyridine rings towards electrophilic attack.[218] Hence a direct bromination of **201** is unlikely to yield any of the desired 4-brominated pyridine **406**. Considering the influence of the pyridine ring on the position of attack of the bromine electrophile on the phenyl ring, it would be expected that substitution would occur in the *meta*-position as the electron-withdrawing pyridine substituent deactivates the phenyl ring to electrophilic substitution, the *meta*-positions being the least deactivated.[219] The expected product of such a reaction would thus be the desired 3'-brominated compound, **407**. Note also that protonation of the pyridine nitrogen, as would be expected if the reaction were carried out in acidic media, would lead to further deactivation of the system.

Despite the absence of any reported attempts to brominate **201**, a number of different procedures for the bromination of deactivated aromatic substrates have been described in the literature and several of these reactions were carried out. The reactions produced a variety of mono- and di-brominated compounds (scheme 4.1). For each reaction the product mixture was analysed by ^{1}H NMR spectroscopy in order to determine its composition. The product mixture for one of the reactions was

chromatographically separated to enable the complete characterisation of a di-brominated 2-phenylpyridine.

Investigation of the bromination of **201** commenced with the reaction of this substrate with bromine and iron powder in glacial acetic acid solution.[220] This reaction (table 4.1, A) gave a quantitative return of unreacted **201**.



201 **407** **408** **409** **410**

Scheme 4.2

Table 4.1 Composition of the product mixture obtained upon attempted bromination of **201** under a variety of reaction conditions

RXN.	*CONDITIONS*	**201**	**407**	**408**	**409**	**410**
A	$Br_2/Fe/CH_3CO_2H$	100	—	—	—	—
B	$Br_2/SbCl_5/ClC_2H_4Cl$	89	trace	11	—	—
C	Br_2/Ag_2SO_4/aq. H_2SO_4 (16M)	12	16	36	26	10
D	$KBrO_3$/aq. H_2SO_4 (6M)	100	—	—	—	—
E	$KBrO_3$/aq. H_2SO_4 (9M)	39	18	24	<5	5
F	$KBrO_3$/aq. H_2SO_4 (12M)	100	—	—	—	—

The bromination of deactivated aromatic compounds in 1,2-dichloroethane with the mixed halogen BrCl formed *in situ* by the interaction of antimony(V) chloride and bromine has been reported.[221] Reaction of **201** under these conditions (table 4.1, B) gave, after work-up, an oil containing 89% unreacted starting material and only a trace of the desired product **407**, with the remaining 11% being the *para*-brominated product, 2-(4-bromophenyl)pyridine (**408**).

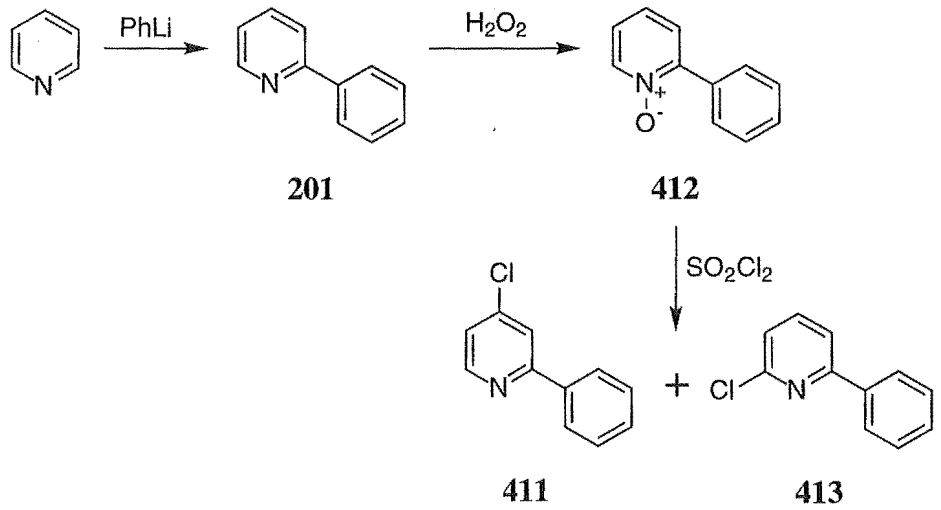
Halogenations of aromatic compounds bearing an electron-withdrawing group have traditionally been carried out under severe conditions involving high temperatures and/or strong electrophilic catalysts with the silver(I) salt-catalysed bromination reaction in concentrated acid being an example. As part of the investigation **201** was treated with bromine in aqueous sulfuric acid in the presence of silver sulfate[222] (table 4.1, C) to give, after work-up, a small quantity of an oil containing four different brominated products, namely: **407** (16%); **408** (36%) and the two dibrominated compounds 2-(2,5-dibromophenyl)pyridine (**409**) (26%) and 2-(3,4-dibromophenyl)pyridine (**410**) (10%), with the remaining 12% being unreacted **201**.

Potassium bromate in sulfuric acid has been in use as a brominating agent since 1875 and the reaction has been the subject of investigations to establish the identity of the attacking species which is believed to be hypobromous acid.[223,224] Reaction of **201** with potassium bromate in 65% sulfuric acid (table 4.1, E) gave, after work-up, an oil in good yield which contained the four brominated products previously observed in the following proportions: **407** (18%); **408** (24%); **409** (<5%) and **410** (5%) with 39% being unreacted **201**. Separation of this mixture by radial chromatography afforded a pure sample of **410** which was fully characterised.

The yield of *meta*-bromonitrobenzene when nitrobenzene is brominated using this procedure has been shown to be dependent upon the sulfuric acid concentration.[224] When the above reaction of **201** was repeated with sulfuric acid concentrations of 38% (table 4.1, D) and 85% (table 4.1, F) a quantitative return of unreacted starting material was obtained.

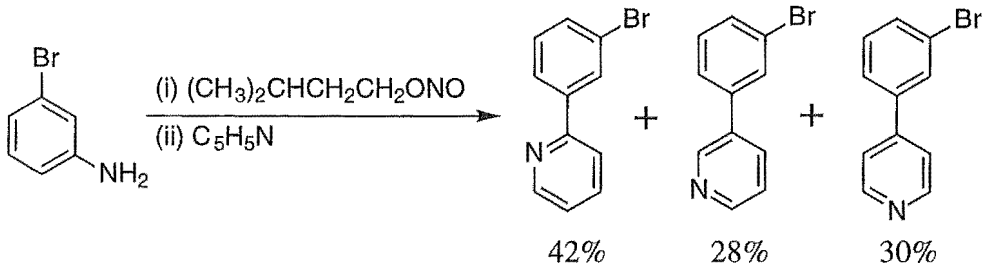
Having established that the direct bromination of **201** did not offer a convenient method for the preparation of **406** or **407**, the preparation of the required halogenated precursors by other means was necessary. Whilst there is no straight-forward method for the synthesis of **406**, the preparation of its chlorinated analogue, 4-chloro-2-phenylpyridine (**411**), in good yield from **201** *via* the corresponding 1-oxide is well-known.[225,226]

Reaction of pyridine with phenyllithium gave **201**[227] in satisfactory yield, with the reaction giving a small amount of a by-product identified as 4,4'-bipyridine. Treatment of an acetic acid solution of **201** with hydrogen peroxide gave 2-phenylpyridine 1-oxide (**412**)[228] which was then treated with sulfuryl chloride to give **411** contaminated by a small amount of 6-chloro-2-phenylpyridine (**413**) (scheme 4.3).[226] The required **411** was separated from the mixture by treatment with alcoholic picric acid followed by liberation of the free base with aqueous sodium hydroxide solution.



Scheme 4.3

The previously reported preparations of **407** involve the treatment of diazotised 3-bromoaniline with pyridine and separation of the three resultant isomeric (3-bromophenyl)pyridines.[216,217] Diazotisation of 3-bromoaniline with nitrous acid[228] followed by addition to pyridine gave, after work-up, a small quantity of the three (3-bromophenyl)pyridines contaminated by unreacted 3-bromoaniline and other 3-bromosubstituted aromatic species. Separation of this oil by radial chromatography afforded a pure sample of **407**, which was fully characterised. The reaction was repeated using isoamyl nitrite as the diazotising agent[217] to give, after work-up and column chromatographic separation, **407** in satisfactory yield (scheme 4.4).



407

Scheme 4.4

With the preparation of **411** and **407**, the halogenated precursors of **402** and **403**, accomplished, attention turned to the development of a coupling procedure that would give the two bis-cyclometallated ligands in satisfactory yield.

In earlier research, the coupling of **411** to give **402** using zinc in the presence of triphenylphosphine to reduce $NiCl_2(PPh_3)_2$ to $Ni^0(PPh_3)_4$ in DMF (the same procedure that was used to prepare **401**) was attempted.[208] This gave a poor yield of **402**. This method was repeated, with an ammoniacal work-up[204] replacing the cyanide demetallation of the earlier method, using **407** as the starting material to give a small quantity of **403**. It was apparent that, whilst the nickel(0)-catalysed coupling strategy was giving the required products, the procedure required some modification to increase the yield of coupled product.

"Nickel Complex Reducing Agents" have been known for some time and contain low oxidation state metal species.[214] Recently these reagents have been used for the preparation of a wide variety of biheterocyclic compounds by the coupling of heterocyclic halides.[210] The investigation of these as potential coupling reagents for the two aromatic halides seemed worthwhile. The coupling procedure using the reagent formed from *tert*-butanol, sodium hydride, triphenylphosphine and nickel acetate in DME[210] was carried out using 2-chloropyridine as a model substrate. This reaction gave no bipy (the expected coupling product) and the reaction was repeated with nickel acetate that had been dried by heating under reduced pressure. This reaction also gave no bipy and the method was not pursued further.

A modified procedure for the coupling of aryl halides based on that used to prepare **401** has been published and this method appears to have several advantages as no additional triphenylphosphine is added during catalyst preparation, assisting in the separation of the products once the reaction is complete and THF is used as the solvent rather than the higher boiling solvent DMF.[211] The method differs from that used to prepare **401** as $NiBr_2(PPh_3)_2$, rather than $NiCl_2(PPh_3)_2$, is used as the catalyst precursor and the reduction by zinc is carried out in the presence of tetraethylammonium iodide. When this method was trialled, again using 2-chloropyridine as the model substrate, a quantitative conversion to bipy was observed in the crude reaction product, and it seemed that a more satisfactory coupling procedure had been found.

Similar reactions of **411** and of **407** proceeded smoothly to give **402** and **403**, respectively, with the yield of both reactions being approximately 50%. Both of the ligands were fully characterised, but the observed melting point of **402**, 112-113.5°C, differs quite markedly from those reported previously for this compound, *viz* 190°C[201] and 170-173°C.[202] Given the absence of additional supporting evidence for the formulation of the compound as **201** in these previous reports, doubts must remain as to which compound had actually been isolated.

Reaction of **402** with one equivalent of lithium tetrachloropalladate in methanol at room temperature gave the monometallated chloro-bridged complex, $[(\mathbf{402}\text{-H})Pd(\mu\text{-Cl})]_2$ in quantitative yield and this was converted to the monomeric acetylacetonate complex, (**402**-H)Pd(acac) (**413**), by ligand exchange with thallium acetylacetonate in chloroform (scheme 4.5). Microanalysis confirmed this formulation with the addition of one third of a chloroform molecule per molecule of complex. Reaction of **403** under similar conditions failed to give the analogous monometallated complex.

In addition to microanalysis, the monocyclopalladated complex, **413**, was fully characterised by FAB mass spectrometry, IR and ^1H and ^{13}C NMR spectroscopy. When compared to the ^1H NMR spectrum of the free ligand, **402**, (figure 4.1a), the spectrum of **413** (figure 4.1b) clearly demonstrates that cyclopalladation has occurred.

The spectrum for **413** is more complex than that of **402**, as single cyclopalladation of the ligand renders the two phenylpyridine subunits inequivalent. The spectrum of the complex was assigned using techniques described in previous chapters, extensive use being made of 1D-TOCSY experiments to assign resonances to specific positions in the isolated spin systems. The NMR characterisation of **413** was completed with the acquisition of a ^{13}C NMR spectrum and its assignment by way of an HMQC experiment.

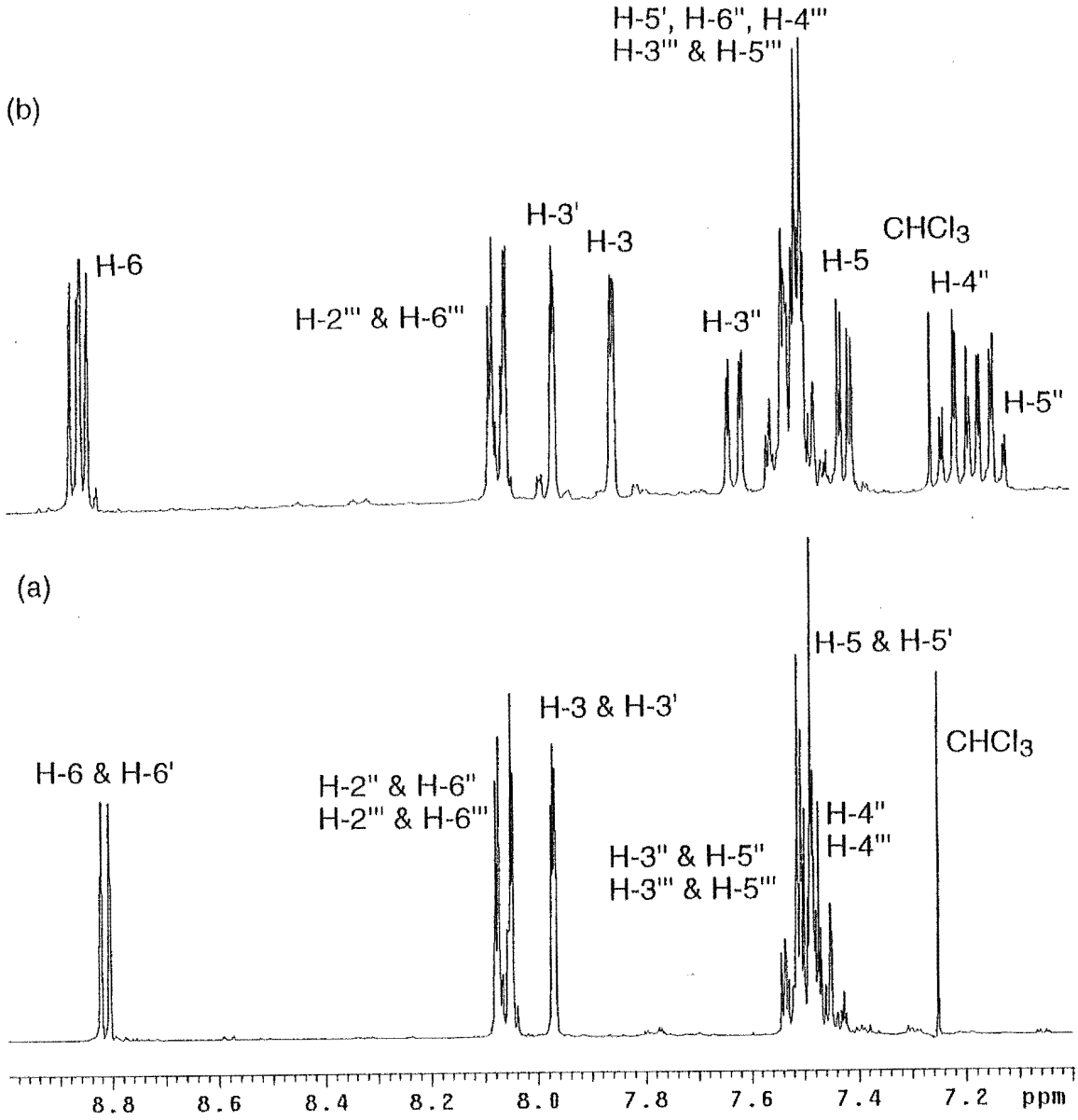
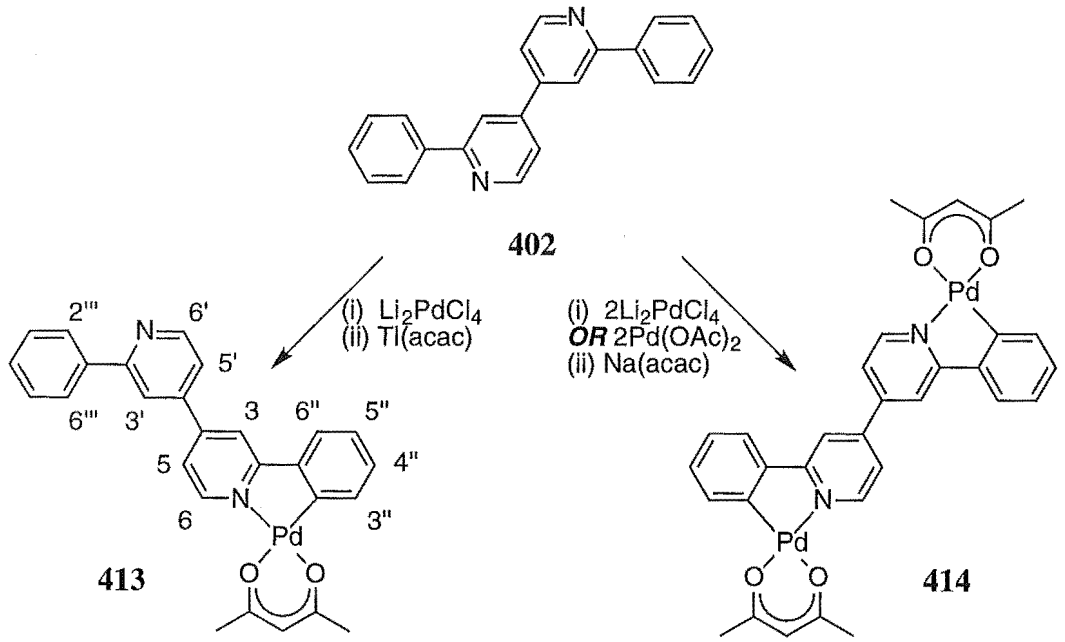


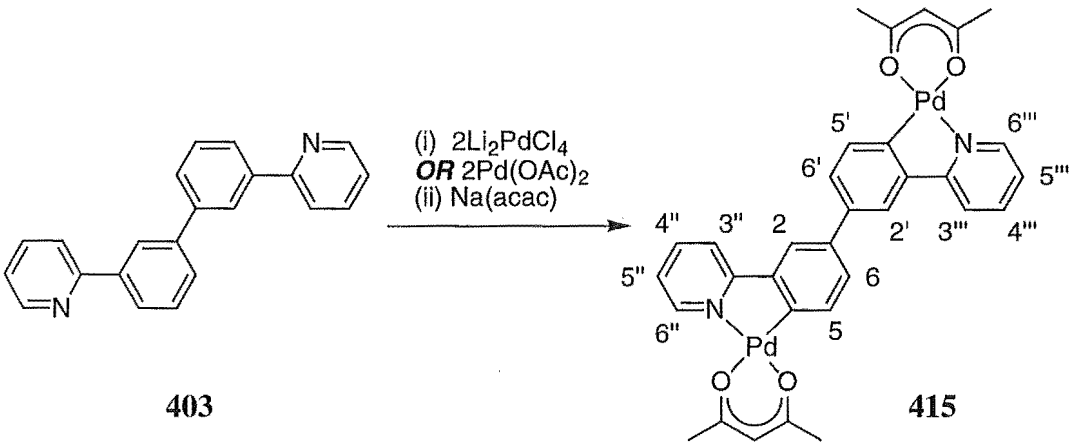
Figure 4.1 (a) ^{1}H NMR spectrum of **402**

(b) Aromatic region of the ^{1}H NMR spectrum of **413**, the monocyclopalladated complex of **402**



Scheme 4.5

Reaction of both ligands with palladium acetate in refluxing acetic acid, followed by acetate-chloride metathesis with lithium chloride, gave the expected bis-cyclometallated chloro-bridged complexes $[(\mathbf{402}\text{-}2H)(Pd(\mu\text{-}Cl))_2]_x$ and $[(\mathbf{403}\text{-}2H)(Pd(\mu\text{-}Cl))_2]_x$. These complexes could also be prepared by reaction of the ligands with lithium tetrachloropalladate in refluxing methanol. Ligand exchange with sodium acetylacetonate afforded the bis-palladium(acac) complexes, (**402**-2H)(Pd(acac))$_2$ (**414**) (scheme 4.5) and (**403**-2H)(Pd(acac))$_2$ (**415**) (scheme 4.6).



Scheme 4.6

Both **414** and **415** were fully characterised, although a ^{13}C NMR spectrum was not acquired for the former complex due to its low solubility. The ^{1}H NMR spectrum

of **415** (figure 4.2b) shows that the equivalence of the two phenylpyridine subunits in the ligand (figure 4.2a) has been maintained. In addition, the resonances in the ^1H NMR spectrum of **415** exhibit the coupling pattern expected of an *ortho*-disubstituted phenyl ring, confirming that the ligand has been doubly cyclopalladated.

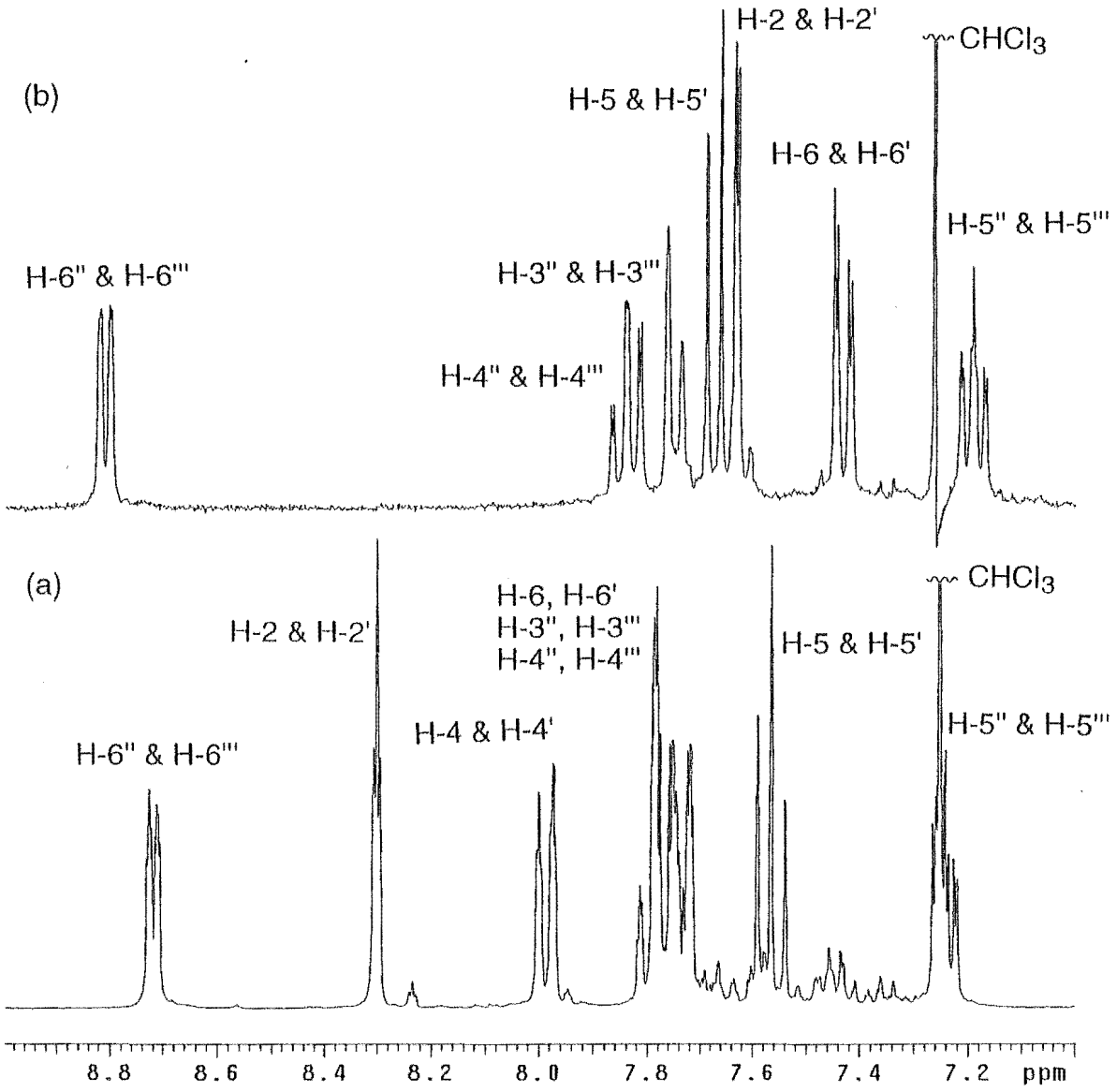


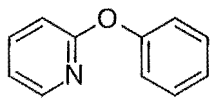
Figure 4.2 (a) ^1H NMR spectrum of **403**

(b) Aromatic region of the ^1H NMR spectrum of **415**, the doubly cyclopalladated complex of **403**

Exhaustive attempts to produce crystals of **414** and **415**, suitable for single crystal X-ray structure determination, were unsuccessful and, therefore, the intermetallic distances and the torsional angles about the central inter-ring bonds in

these complexes are unknown. The electrochemistry of these complexes has not been examined, as the two electron palladium(II)-palladium(IV) couple is less amenable to such studies than the corresponding one electron ruthenium(II)-ruthenium(III) couple. Thus, electrochemical studies, and the determination of the magnitude of metal-metal communication in complexes of **402** and **403**, await the preparation of doubly cycloruthenated complexes.

4.3 POTENTIALLY BRIDGING ANALOGUES OF 2-PHENOXYPYRIDINE AND 2-PHENYLTHIOPYRIDINE



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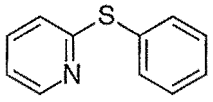
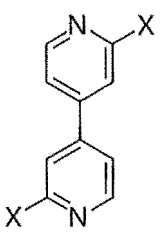
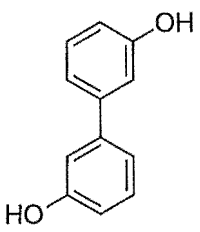


233

Having successfully cyclopalladated both 2-phenoxypyridine (**232**) and 2-phenylthiopyridine (**233**), the possibility of preparing potentially doubly metallated analogues of these ligands was considered. The most obvious synthetic route to such compounds is by the nucleophilic substitution of appropriate halogenated precursors with the phenoxide or thiophenoxide anions, the route that was used to prepare both **232** and **233**. To prepare quaterpyridine-type analogues in this manner would require the precursors 2,2'-dihalo-4,4'-bipyridine (**416**) and/or 3,3'-dihydroxybiphenyl (**417**) and its sulphur analogue (**418**), none of which are readily available. Hence attention turned to other structures that would permit the linking of two **232**- or two **233**-like subunits that would incorporate the essential feature of two N-donors with 2-phenoxy or 2-phenylthio substituents attached.



416



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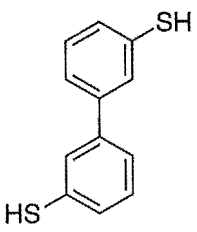
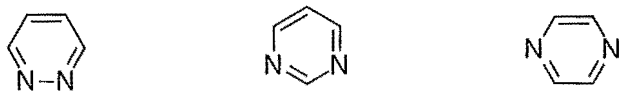


418

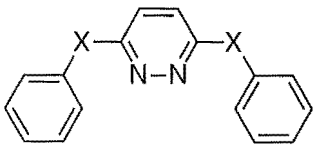
The diazines—pyridazine; pyrimidine and pyrazine (figure 4.3)—offer the possibility of linking these subunits through a common central ring which includes both of the N-donor atoms.



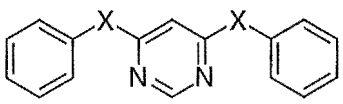
pyridazine pyrimidine pyrazine

Figure 4.3

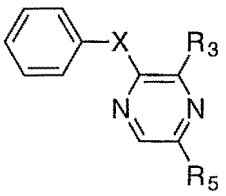
Addition of the required substituents to the diazine ring gives the structures 3,6-diphenoxypyridazine (**419**), 4,6-diphenoxypyrimidine (**420**), 2,3-diphenoxypyrazine (**421**) and 2,5-diphenoxypyrazine (**422**) and their analogues, 3,6-bis(thiophenyl)pyridazine (**423**), 4,6-bis(thiophenyl)pyrimidine (**424**), 2,3-bis(thiophenyl)pyrazine (**425**) and 2,5-bis(thiophenyl)pyrazine (**426**), where sulfur atoms replace the oxygen atoms in these compounds.



419 X=O
423 X=S

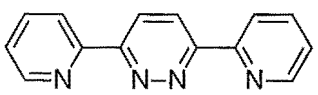


420 X=O
424 X=S



421 X=O, R_3=OPh, R_5=H
425 X=S, R_3=SPh, R_5=H
422 X=O, R_3=H, R_5=OPh
426 X=S, R_3=H, R_5=SPh

Such ligands would be cyclometallated analogues of the well-studied multidentate bridging ligands 3,6-bis(2-pyridyl)pyridazine (**427**), 4,6-bis(2-pyridyl)-pyrimidine (**208**), 2,3-bis(2-pyridyl)pyrazine (**428**) and 3,5-bis(2-pyridyl)pyrazine (**429**).[51]



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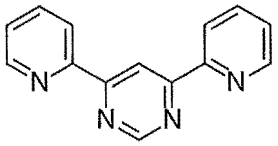

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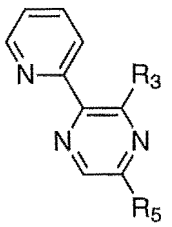
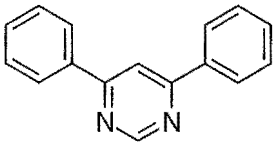


428 R_3=2-py, R_5=H
429 R_3=H, R_5=2-py

Indeed, 4,6-diphenylpyrimidine (**209**),[110] 2,3-diphenylpyrazine (**430**)[111] and 2,5-diphenylpyrazine (**431**),[229] which are also analogues of these bridging binuclear coordinating ligands, have been prepared and doubly cyclometallated.



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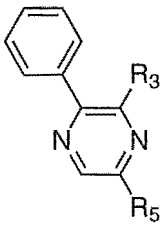
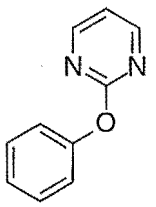


430 R_3=Ph, R_5=H
431 R_3=H, R_5=Ph

A search of the literature revealed that both 3,6-diphenoxypyridazine (**419**)[230,231] and 3,6-bis(phenylthio)pyridazine (**423**)[232] are known compounds. Although there have been several phenoxypyrimidines reported in the literature, for example 2-phenoxypyrimidine (**432**),[233,234] 4-methyl-2-phenoxypyrimidine (**433**),[233,234] 4,6-dimethyl-2-phenoxypyrimidine (**434**)[234,235] and the bis-ether, 2,4-diphenoxypyrimidine (**435**),[236] the preparation of **420** has not previously been described.



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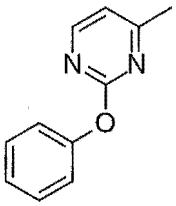

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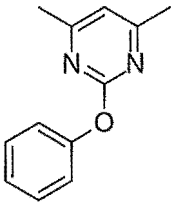

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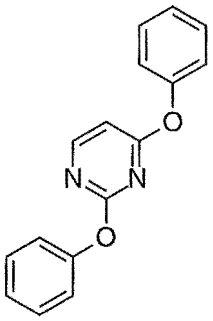
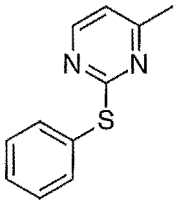


435

Similarly, although the synthesis of 4,6-bis(phenylthio)pyrimidine (**424**) has not previously been reported, the preparations of several other (phenylthio)pyrimidines, for example 2-(phenylthio)pyrimidine (**436**)[237] and 4-phenyl-2-(phenylthio)pyrimidine (**437**),[238] have been described.



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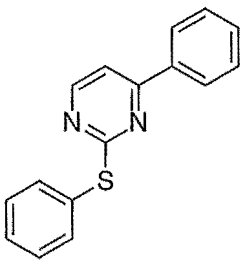
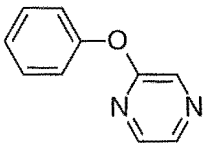


437

A search for phenoxy- and (phenylthio)pyrazines yielded preparations for phenoxypyrazine (**438**)[239] and for 3-methyl-2-phenoxy- (**439**) and 3-methyl-2-(phenylthio)pyrazine (**440**)[240] whilst reports of diphenoxypyrazines are confined to a paper (no preparations given) which describes some properties of 2,6-diphenoxypyrazine (**441**), an isomer which would be unable to doubly cyclometallate, in addition to a number of other phenoxy- and (phenylthio)pyrazines, all of which have other substituents on the pyrazine nucleus and some of which have substituents on the phenyl ring of the phenoxy and phenylthio substituents.[241]



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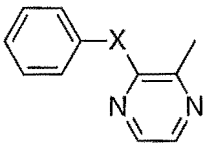
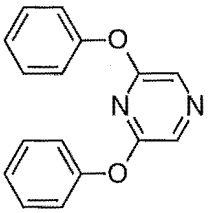


439 X=O
440 X=S



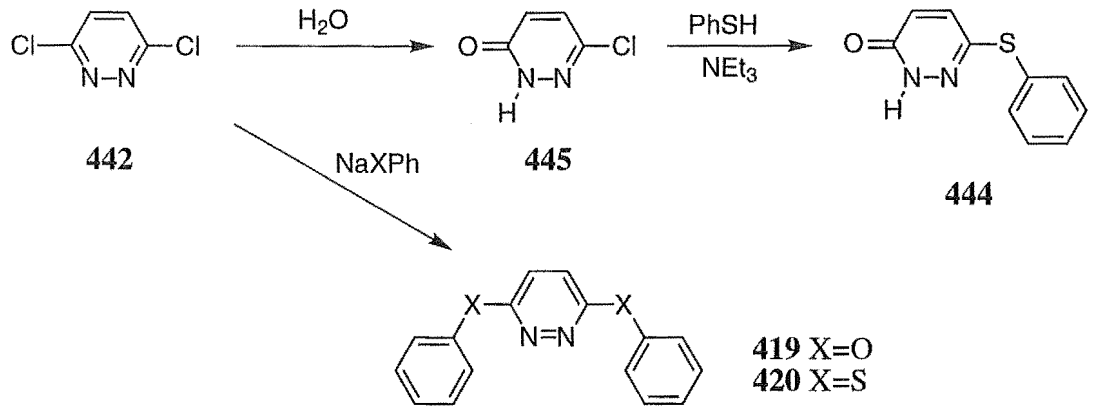
441

The literature preparations for the known phenoxy- and (phenylthio)diazines mentioned above do involve the nucleophilic substitution of the appropriate chlorodiazine with phenoxide or thiophenoxide anions and, given the ready availability of both 3,6-dichloropyridazine (**442**) (scheme 4.7) and 4,6-dichloropyrimidine (**443**) (scheme 4.8) and the absence of a convenient preparation of either 2,3- or 2,5-dihalopyrazine, attention was focused on the preparation of the pyridazine and pyrimidine ligands.

In addition to providing a convenient route to potentially doubly cyclometallating ligands, the method of preparation of these ligands offered, through the preparation of unsymmetrical phenoxy(thiophenyl)diazines, the potential to further

investigate the regioselectivity of the cyclometallation reaction by establishing the relative ease of cyclometallation of a thiophenoxide system, with respect to a phenoxide system, when both are in a ß-arrangement with similar nitrogen donor atoms in the same ligand. Such unsymmetrical ligands could be prepared by the reaction of the dichlorodiazine with one equivalent of phenoxide anion followed by isolation of the mono-ether and its subsequent reaction with thiophenoxide anion or vice versa.

The first attempt to prepare 3,6-bis(thiophenyl)pyridazine (**423**) was by the reaction of **442** with thiophenol in the presence of triethylamine, in a reaction analogous to that used to prepare **233** from 2-chloropyridine.[140] Examination of the ^{1}H NMR spectrum of the product from this reaction revealed that the product was not that expected, the pattern of pyridazine proton signals showing an unsymmetrically substituted system and the presence of a broad singlet at 12.56 ppm suggested a signal due to an N-H moiety. Mass spectrometry and microanalysis confirmed the identity of this product as the hitherto unknown compound 6-phenylthiopyridazin-3(2*H*)one (**444**) (scheme 4.7). The melting point of the starting material employed in this reaction (126-136°C) indicated that the **442** (lit.[242] 68-69°C) had hydrolysed during storage to 3-chloropyridazin-6(1*H*)one (lit.[243] 138-139°C).

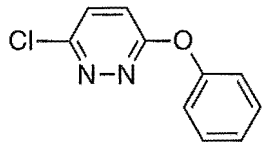


Scheme 4.7

The bis-thioether (**423**) was obtained by the reaction, in ethanol, of sodium thiophenoxide with fresh **442** according to the previously published procedure (scheme 4.7).[232] The compound was fully characterised using NMR and IR spectroscopy and mass spectrometry.

The corresponding bis-ether, 3,6-diphenoxypyridazine (**419**), was obtained by the reaction of **442** with sodium phenoxide according to the literature procedure (scheme 4.7).[230] Again, this compound was fully characterised using the techniques described for the bis-thioether. Worthy of note is the fact that all signals in the ^1H NMR spectrum of the ligand in $CDCl_3$ are broadened, with the spectrum in d_6-DMSO being broadened to an apparently lesser extent and the ^{13}C NMR spectra in both solvents seemingly unaffected. Similar broadening has been observed in the ^1H NMR spectrum of 1,4-bis(3-pyridoxy)benzene, an isoelectronic analogue of **419**.[244]

Tamura and Jojima[231] report that reaction of **442** with one equivalent of sodium phenoxide in refluxing benzene gives only the mono-ether, 3-chloro-6-phenoxypyridazine (**446**), and that disubstituted **419** forms only when the reaction is carried out at higher temperature in refluxing toluene. In addition, the authors state that **446** and **419** can be easily separated from one another by recrystallisation from ether or ethanol. However, when the reaction in benzene was carried out the product mixture was found to contain approximately 15% **419** and recrystallisation of this mixture failed to enrich the proportion of mono-ether. Unlike **419** (*vide supra*), the signals in the NMR spectra of **446** show no apparent broadening.

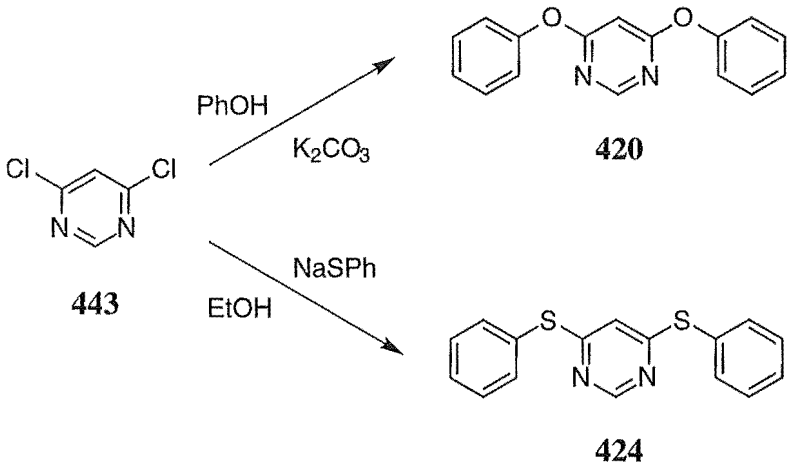


446

In a reaction analogous to that used to prepare **232**,[135] phenol and 4,6-dichloropyrimidine (**443**) were melted together in the presence of potassium carbonate to give, after work-up, the new bis-ether 4,6-diphenoxypyrimidine (**420**) in excellent yield (scheme 4.8). The compound was fully characterised by microanalysis, mass spectrometry and IR and NMR spectroscopy, the NMR spectra showing no apparent broadening.

Using a procedure analogous to that which gave **423**,[232] the corresponding bis-thioether, 4,6-bis(phenylthio)pyrimidine (**424**), was prepared in satisfactory yield

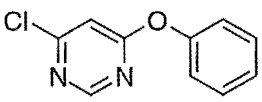
from **443** and sodium thiophenoxide (scheme 4.8). This ligand was also fully characterised using the techniques described for the bis-ether.



443 **420** **424**

Scheme 4.8

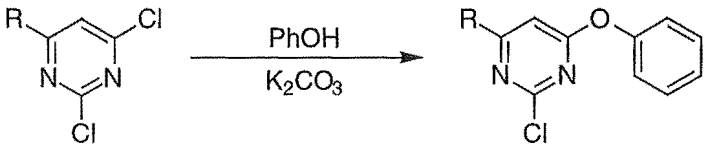
As with the pyridazine series, the preparation of the mono-ether, 4-chloro-6-phenoxypyrimidine (**447**), from the dichlorodiazine, **443**, was attempted. When **443** was melted together with excess phenol in the presence of one equivalent of potassium carbonate an equimolar mixture of **447** and **420** was obtained, as determined by ^{1}H NMR analysis of the crude product. Reaction in refluxing benzene with one equivalent of sodium as the base gave a greater proportion of **447** in the product mixture, the molar ratio **447**:**420** being approximately four:one. As with the analogous pyridazine ethers, repeated attempts to separate the two ethers by recrystallisation were unsuccessful.



447

The only report of mono-(phenoxy)ethers being prepared from dichloropyrimidines is that of 2-chloro-4-phenoxypyrimidine (**448**) and 2-chloro-4-phenoxy-6-methylpyrimidine (**449**), from 2,4-dichloropyrimidine (**450**) and 2,4-dichloro-6-methylpyrimidine (**451**) respectively (scheme 4.9). In these reactions the successful preparation of the mono-ether (and the small amount of bis-ether observed in the crude product) can be attributed to the difference in susceptibility to nucleophilic

attack between the 2-chloro substituent and the more reactive 4-chloro substituent,[236] such a difference not existing between the two equivalent chlorine atoms in **443**.



450 R=H
451 R=CH_3

448 R=H
449 R=CH_3

Scheme 4.9

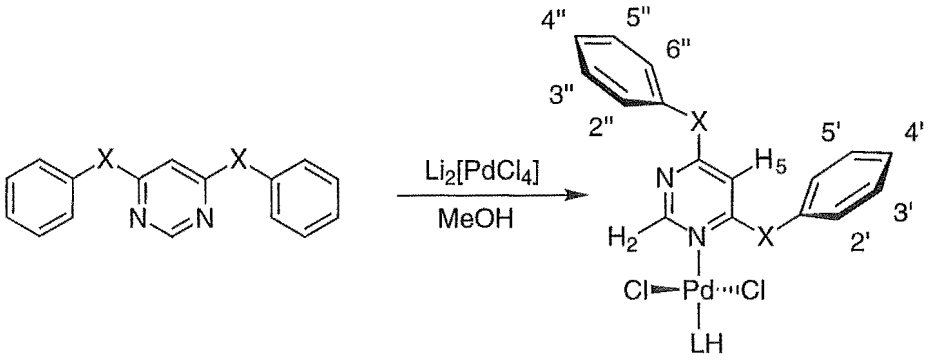
Investigation of the complexation chemistry of the bis-ether ligands **419** and **420** and of the bis-thioether ligands **423** and **424** began with their reactions with lithium tetrachloropalladate in methanol. When reacted under these conditions all four ligands gave coordination complexes, with no cyclometallation observed.

Reaction of the pyridazine bis-ether, **419**, with lithium tetrachloropalladate gave Pd(**419**)$_2$Cl$_2$ in excellent yield. The complex was recrystallised from nitromethane and is insoluble in $CDCl_3$ but is soluble in d_6-DMSO. However, it appears that this solvent displaces the ligand as both the ^{1}H and ^{13}C NMR spectra of the solution are indistinguishable from that of the free ligand and, therefore, the complex was characterised by microanalysis and IR spectroscopy.

The corresponding bis-thioether, **423**, upon reaction with lithium tetrachloropalladate, gave Pd(**423**)$_2$Cl$_2$ in excellent yield. The complex was recrystallised from chloroform by the diffusion of petroleum ether vapour; however the complex is insufficiently soluble in $CDCl_3$ to obtain NMR spectra. As with the bis-ether coordination complex discussed above, this complex is soluble in d_6-DMSO but, again, the solvent displaces the pyridazine ligands to give ^{1}H and ^{13}C NMR spectra identical to those of the free ligand. Hence the complex was characterised by microanalysis and IR spectroscopy.

Reaction of the pyrimidine bis-ether, **420**, with lithium tetrachloropalladate gave, in excellent yield, a yellow solid which was recrystallised from nitromethane and toluene to give yellow needle crystals formulated by microanalysis as Pd(**420**)$_2$Cl$_2$

(**452**) with the inclusion of two thirds of a molecule of toluene per molecule of complex. This complex is soluble in chloroform and examination of both ^{1}H and ^{13}C NMR spectra confirm the above formulation as they show the presence of two inequivalent and non-cyclometallated phenyl rings. The largest coordination induced shift in the ^{1}H NMR spectrum of the complex, with respect to that of the free ligand, is for H-2 of the pyrimidine ring, which shifts downfield by 0.39 ppm upon coordination of the palladium, whilst H-5 of the pyrimidine ring shifts upfield by 0.27 ppm. These shifts are consistent with the expected *trans* geometry of the complex (shown in scheme 4.10, with one pyrimidine ligand omitted for clarity) as H-2 is deshielded due to the influence of the nearby chloro ligand, whilst upon coordination the phenyl ring of the phenoxy substituent adjacent to the coordinating nitrogen atom twists away from the palladium atom and H-5 is thus affected by the shielding ring current of this group.



420 X=O
424 X=S

452 X=O, LH=**420**
453 X=S, LH=**424**

Scheme 4.10

The corresponding complex, Pd(4,6-bis(phenylthio)pyrimidine)$_2$Cl$_2$ (**453**), was obtained in excellent yield as an analytically pure yellow powder from the reaction of lithium tetrachloropalladate with two equivalents of the bis-thioether ligand, **424** (scheme 4.10). The same complex was obtained in poorer yield and of lower purity when the reaction was repeated with an equimolar ratio of palladium to ligand.

The ^{1}H NMR spectrum of this complex (figure 4.4) exhibits temperature dependent behaviour, and at 23°C the resonances are broadened. Of particular note is the appearance of the signals for H-2 and H-5 of the pyrimidine ring as broadened doublets with a separation of 9.3 Hz for H-2 and of 17.3 Hz for H-5. The broadening is

also seen in the ^{13}C NMR spectrum, and C-2 and C-5 again appear as doublets with the signals for the phenyl rings showing two peaks for each position in a ratio of two:one. As the temperature is increased to 53°C the individual signals for H-2 and H-5 coalesce and appear as singlets, whilst one signal due to a pair of *ortho* protons on one of the phenyl rings becomes discernible, the rest of the phenyl protons forming one large overlapping absorption from which the individual shifts could not be resolved. In the ^{13}C NMR spectrum at 53°C the signals corresponding to C-2 and C-5 also appear as singlets and the pairs of resonances for each of the phenyl carbons are of approximately equal intensity. The chemical shifts for H-2 and H-5 show coordination induced shifts of the same sign as their counterparts in the analogous 4,6-diphenoxypyrimidine complex (**452**), with H-2 being shifted downfield by 0.22 ppm and H-5 upfield by 0.16 ppm, suggesting that the complexes have the same, *trans*, stereochemistry.

The proposed explanation for the observed temperature dependence of the NMR spectra of **453** is that it is the result of the an equilibrium between *syn* and *anti* rotamers, as has been discussed for the corresponding complexes of both 2-phenoxypyridine (**232**) and 2-phenylthiopyridine (**233**), and other ligands (*vide supra*). It is noteworthy that, whilst coalescence temperatures for the resonances in the spectrum of the complex of **203** could not—due to instrument and solution temperature limitations—be determined, those for **453** are approximately 28°C for H-2 and 38°C for H-5. In addition, the signals for the diphenoxypyrimidine complex, **452**, have coalescence temperatures somewhat below 23°C as no broadening of the spectrum (figure 4.5b) is observed at ambient temperature, in contrast to the spectrum of the corresponding **232** complex, the spectrum of which is significantly broadened at the same temperature. Thus, the activation energies for intramolecular rotamerisation for the disubstituted pyrimidine complexes are of somewhat lesser magnitude than those for the corresponding monosubstituted pyridine complexes. The difference between the observed temperature dependence in the spectra of **452** and **453** is expected to be due to the same factors proposed to account for the observed difference in the spectral temperature dependence of the complexes of **232** and **233**, namely; the respective sizes

of the oxygen and sulfur atoms and possible interaction between the palladium and sulfur atoms.

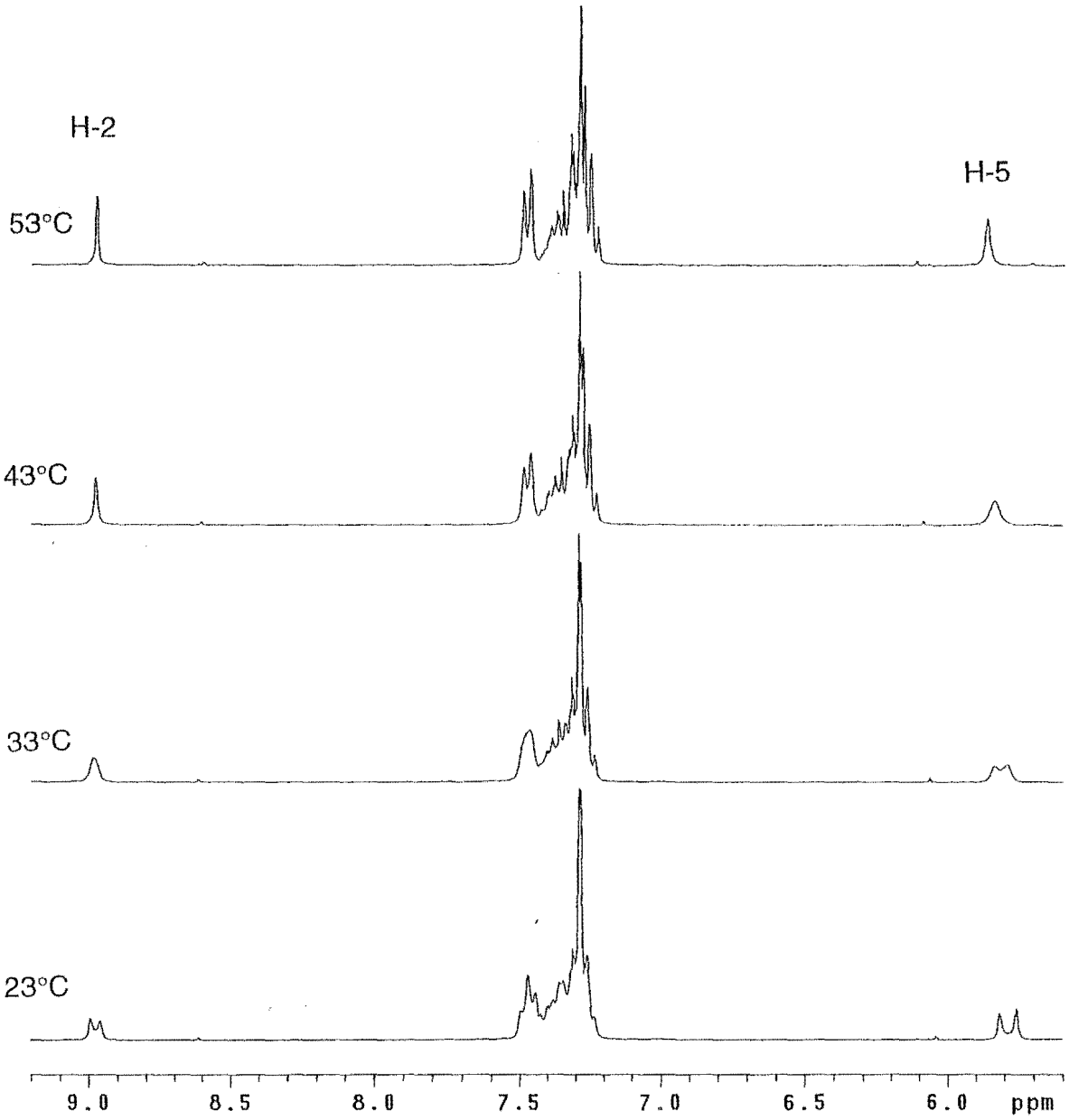


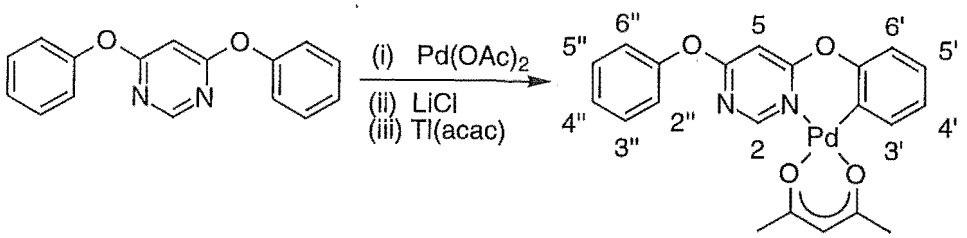
Figure 4.4 Variable temperature ^{1}H spectra of **453**

Having established that reaction with lithium tetrachloropalladate does not lead to cyclometallation of these ligands, their reactions with palladium acetate were investigated as this has been shown to be a more reactive metallating agent.[123] For example, some potentially doubly metallating ligands have been singly metallated with the former reagent, whilst the latter reagent gives the doubly metallated complex.[111]

Refluxing glacial acetic acid has been used as the solvent for such metallations by other researchers, but reaction of the pyridazine and pyrimidine bis-ethers and bis-thioethers under these conditions failed to give any of the desired metallated complexes, as did reaction in acetic acid at room temperature. Attention then turned to other solvents that might facilitate the cyclometallation of these ligands with palladium acetate.

In 1980 Gutierrez *et al.* published a paper that described the cyclometallation of a number of 2-arylpyridines with palladium acetate in refluxing acetic acid and noted that "refluxing chloroform proved to be a better solvent choice."[245] This was presumably due to the higher yields of the acetate-bridged dimer obtained when the reaction was performed in the latter solvent. In an attempt to prepare the cyclopalladated complex the pyrimidine bis-ether, **420**, and palladium acetate were reacted together in chloroform. However, after one day under reflux, ^{1}H NMR examination of a sample of the reaction mixture showed only unreacted ligand.

Another solvent which has been used for cyclometallations by palladium acetate is benzene.[246] Reaction of the pyrimidine bis-ether, **420**, with palladium acetate in benzene under nitrogen gave a mixture of the unreacted ligand (approximately 25% by ^{1}H NMR spectroscopy) and the acetate-bridged dimer, [Pd(**420**-H)OAc]$_2$, which was characterised by ^{1}H NMR spectroscopy to confirm that cyclopalladation had occurred. Acetate-chloride metathesis gave the corresponding chloro-bridged dimer, [Pd(**420**-H)Cl]$_2$, which was fully characterised, a low chloride analysis notwithstanding. Ligand exchange of this dimeric complex with thallium acetylacetonate gave the monomeric palladium acetylacetonate complex, Pd(**420**-H)(acac) (**454**) in good yield as pale yellow plates (scheme 4.11). This complex was fully characterised; however signals corresponding to the quaternary pyrimidine carbons C-4 and C-6 were not observed in the ^{13}C NMR spectrum and, in the ^{1}H NMR spectrum (figure 4.5c), the signals for H-4' and H-5' of the metallated phenyl ring were found to have chemical shifts that were insufficiently separated to allow resolution by available NMR techniques.



420 **454**

Scheme 4.11

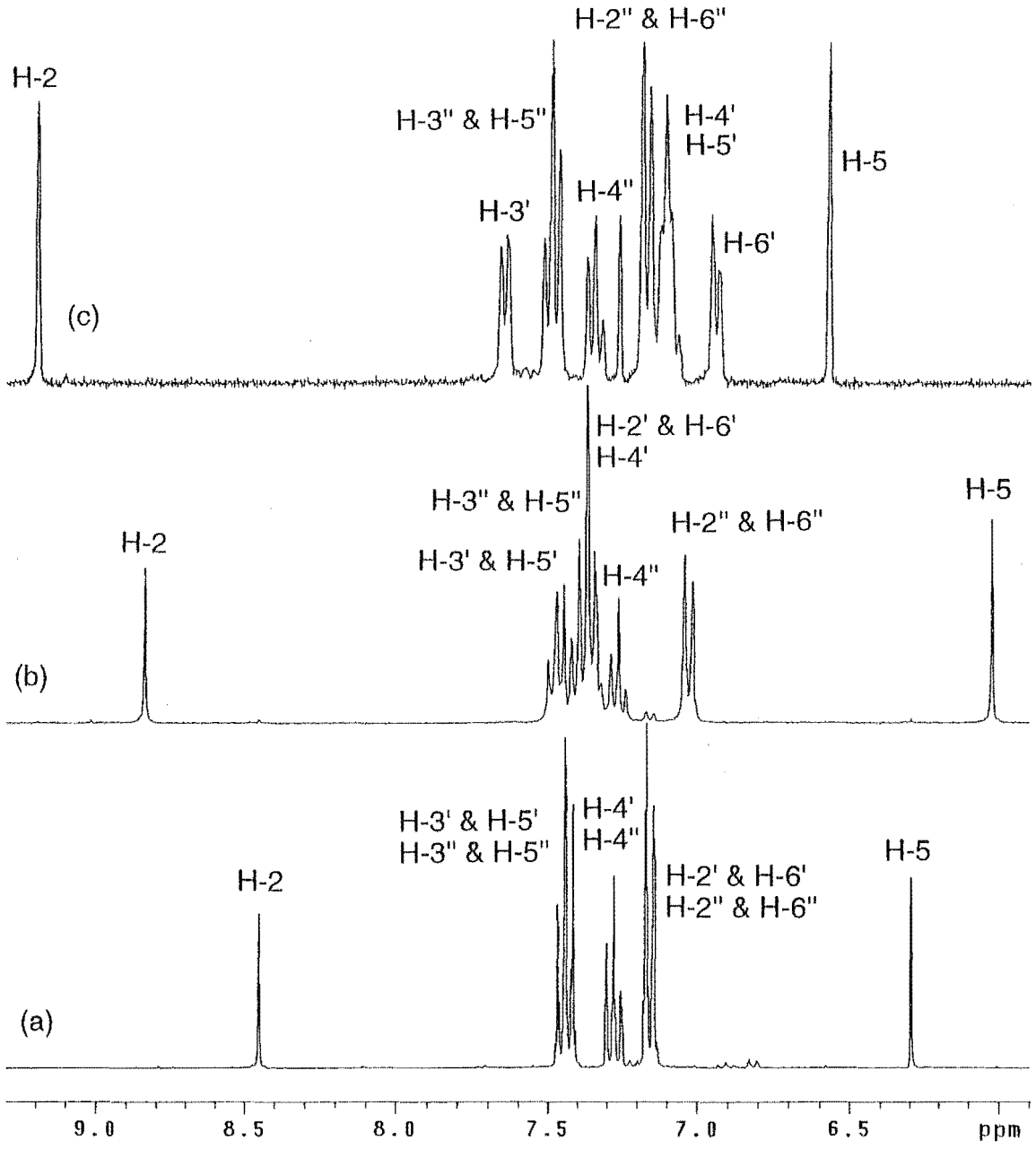


Figure 4.5 (a) ^{1}H NMR spectrum of **420**

(b) ^{1}H NMR spectrum of **452**

(c) Aromatic region of the ^{1}H NMR spectrum of **454**

Reaction of the pyridazine bis-ether, **419**, with palladium acetate in benzene under nitrogen also gave a mixture of the unreacted ligand and the acetate-bridged dimer, [Pd(**419**-H)OAc]$_2$. This mixture was characterised by both ^{1}H and ^{13}C NMR spectroscopy, the overlapping of signals being such that it was difficult to ascertain whether or not the ligand had been cyclometallated on the basis of the ^{1}H NMR spectrum alone.

The corresponding chloro-bridged dimer, [Pd(**419**-H)Cl]$_2$, was prepared by reaction of the acetate-bridged dimer with lithium chloride to give a pale yellow insoluble solid which was characterised by IR spectroscopy. In the reaction of [Pd(**419**-H)Cl]$_2$ with thallium acetylacetonate, pale yellow crystals of the resultant monomeric complex, Pd(**419**-H)(acac) (**455**), suitable for single-crystal X-ray structure determination were obtained in excellent yield directly from diffusion of petroleum ether into a chloroform solution prepared from the filtrate of the reaction mixture. Therefore the crystal structure of this complex, which was also characterised by microanalysis and IR and ^{1}H and ^{13}C NMR spectroscopy, was determined.

Crystal Structure of **455**.

The cyclopalladated complex of 3,6-diphenoxypyridazine crystallises in the orthorhombic space group $P2_12_12_1$, the asymmetric unit of which contains two Pd(**419**-H)(acac) bis-chelate molecules (figure 4.6). This complex represents the first example of a crystallographically characterised structure incorporating a bidentate ligand with a nitrogen donor in a six-membered metallocycle formed from palladation of an aryl ring. Other related structures incorporate tridentate metallated ligands[247-251] or result from aliphatic palladation[252-259] or both.[260-265]

The two independent molecules have bonding geometries that are the same within experimental error but differ in the conformation of the non-metallated phenoxy substituent, the phenoxy and pyridazine ring meanplanes being inclined at 72.7° in one ligand (complex with Pd1) and 63.7° in the other ligand (complex with Pd1A). The

four phenyl and two pyridazine rings are each essentially planar, with the maximum displacement from the plane being 0.023(4) Å for C1'A.

The six-membered metallocycles each exist in a shallow boat conformation: Pd1 and O3 are 0.640(2) and 0.368(3) Å, respectively, above the meanplane defined by N2, C3, C1' and C2'; and Pd1A and O3A are 0.656(2) and 0.347(3) Å, respectively, above the meanplane defined by N2A, C3A, C1'A and C2'A. The cyclometallated phenyl ring is inclined to the pyridazine ring at an angle of 38.6° in one ligand and at 37.0° in the other ligand.

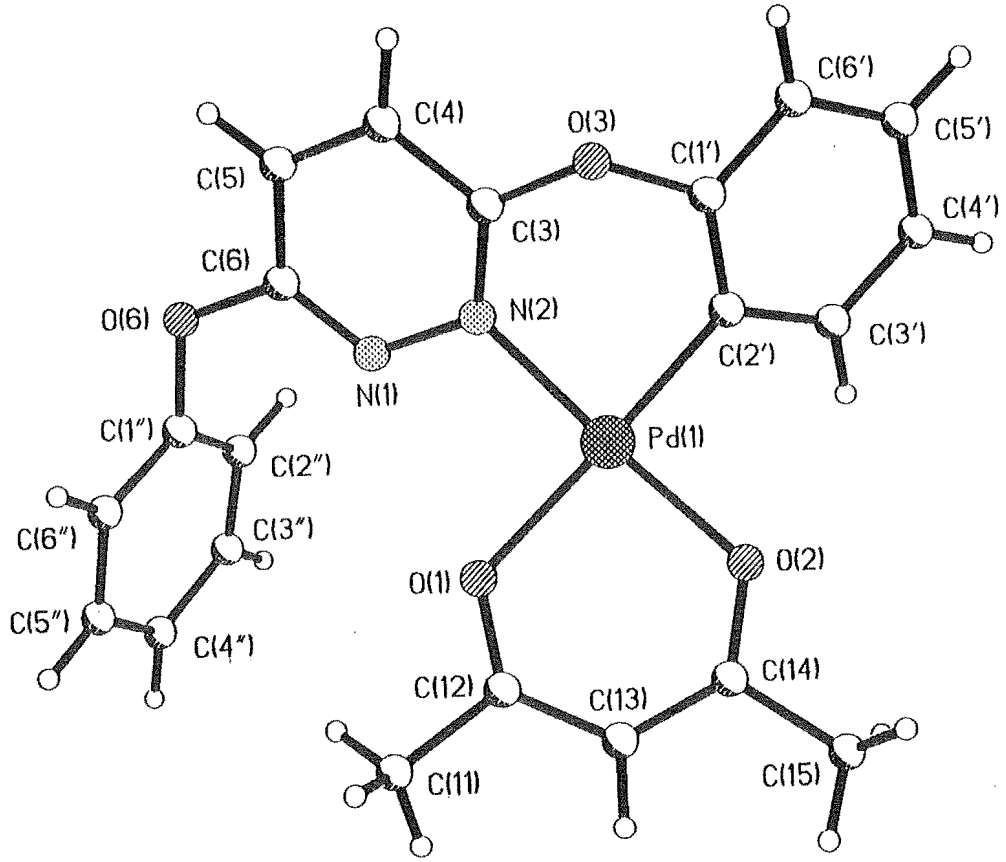


Figure 4.6 Perspective view and atom labelling of one of the two independent molecules in the asymmetric unit of **455**. Selected bond lengths (Å) and angles (°) for the Pd1 and [Pd1A] molecule: Pd1-C2' 1.972(3) [1.974(3)], Pd1-N2 2.012(2) [2.006(2)], Pd1-O1 2.080(2) [2.076(2)], Pd1-O2 2.032(2) [2.018(2)]; C2'-Pd1-N2 87.3(2) [87.6(1)], O1-Pd1-O2 91.66(8) [91.92(7)], C3-O3-C1' 119.5(2) [120.7(2)].

The palladium atoms have approximately square planar coordination to the C,N,O,O donor set and the Pd-C, Pd-N bond lengths are similar to those in related cyclopalladated complexes which incorporate a nitrogen donor in a five-membered metallocycle.[266] There is evidence of a very slight tetrahedral distortion from square planarity around the palladium atoms, as the meanplanes defined by Pd1 (deviation from the plane of -0.005(2) Å), N2 (0.009(3) Å), C2' (-0.007(4) Å), O1 (-0.006(3) Å) and O2 (0.009(3) Å) and by Pd1A (-0.007(2) Å), N2A (-0.008(3) Å), C2'A (0.012(4) Å), O1A (0.011(3) Å) and O2A (-0.008(3) Å) show alternating displacement of the atoms above and below the plane. This is supported by the trans-coordination angles: (178.3(1) and 177.3(1)° for Pd1; 177.8(1) and 177.7(1)° for Pd1A).

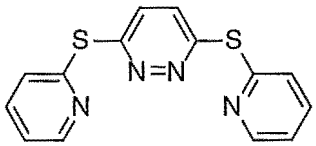
The geometries of the two acetylacetonate subunits are very similar to those that have been determined for related structures.[266] Of particular note is the difference in the Pd-O bond lengths, with those *trans* to carbon being significantly longer than those *trans* to nitrogen, this variation being consistent with those seen in related structures and a reflection of the different *trans* influences of carbanion and nitrogen donors.[266]

Having prepared and characterised the singly cyclopalladated complexes of both the pyridazine and the pyrimidine bis-ethers, the corresponding bis-thioethers, **423** and **424**, were reacted with palladium acetate. The ligands were reacted with palladium acetate both in acetic acid and in benzene, however all attempts to cyclopalladate the bis-thioethers were unsuccessful.

A number of attempts were made to doubly metallate the pyridazine and pyrimidine bis-ethers with palladium acetate in a variety of solvents under a range of conditions but these gave only the singly cyclopalladated complexes.

Studies of 3,6-di-(2-pyridylthio)pyridazine (**456**), the tetradentate (N_4) analogue of the pyridazine bis-ether, **419**, have shown that this ligand predominantly forms binuclear copper(II) complexes in which the two copper(II) ions are bridged by two exogenous bridges in addition to the diazine group.[267-272] Examination of the

structures obtained through X-ray crystallographic studies of these complexes[267-272] shows that formation of a binuclear complex with two six-membered chelate rings connected only through the pyridazine ring would impose considerable strain on the molecule. The observed structures exhibit intermetallic separations of between 3.00 and 3.22 Å and the steric interactions between other ligands attached to the copper atoms would be so great as to preclude the formation of such a complex. For similar structures with five-membered chelate rings, the intermetallic distances are between 3.29 and 3.46 Å and these ligands form structures in which the two copper(II) ions are connected by only one additional exogenous bridge.[272]



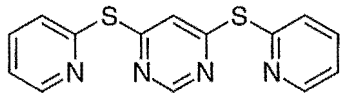
456

A similar study of 4,6-di-(2-pyridylthio)pyrimidine (**457**), an analogue of the pyrimidine bis-ether, **420**, has shown that this ligand forms 1:1 complexes with copper salts.[273] Crystallographic studies reveal that, within these complexes, the potentially tetradentate bridging ligand acts as a tridentate donor, coordinating in a bidentate fashion to one copper ion through a pyrimidine and pyridine nitrogen and acting as a monodentate donor to the other copper ion through the other pyridine nitrogen.[273]

A recent investigation of the reactions of **457** with ruthenium(II) and silver(I) also did not produce bis-bidentate complexes.[274] The ligand forms 1:1 complexes, which were crystallographically characterised, with these metals ions, exhibiting monochelate coordination upon reaction with ruthenium(II) and bridging, triply monodentate coordination upon reaction with silver(I)—the fourth, pyrimidine nitrogen in this complex again uncoordinated.[274]

These reports contrast with that of the analogous, diphenylpyrimidine ligand, **209**, which exhibits bis-bidentate coordination, forming a doubly cyclopalladated complex in which the two five-membered metallocycles are connected through the central pyrimidine ring.[110] The difference in observed mode of coordination between

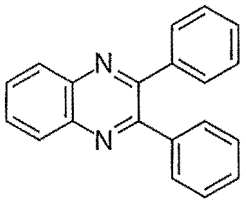
the two ligands is attributed to the formation of six-membered chelate rings in complexes of the bis-thioether, **457**. As a result of this, steric interactions between ancillary ligands on the copper(II) ions and H-2 of the pyrimidine ring and H-6 of the pyridine rings lead to twisting of the bridging ligand, preventing the formation of the second chelate ring due to the inaccessibility of the second pyrimidine nitrogen.[273]



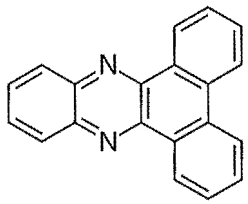
457

The preparation of a complex in which two six-membered chelate rings are connected solely through a disubstituted bis-bidentate pyridazine or pyrimidine bridging ligand is, therefore, yet to be achieved.

4.4 OTHER POTENTIALLY DOUBLY CYCLOMETALLATED LIGANDS



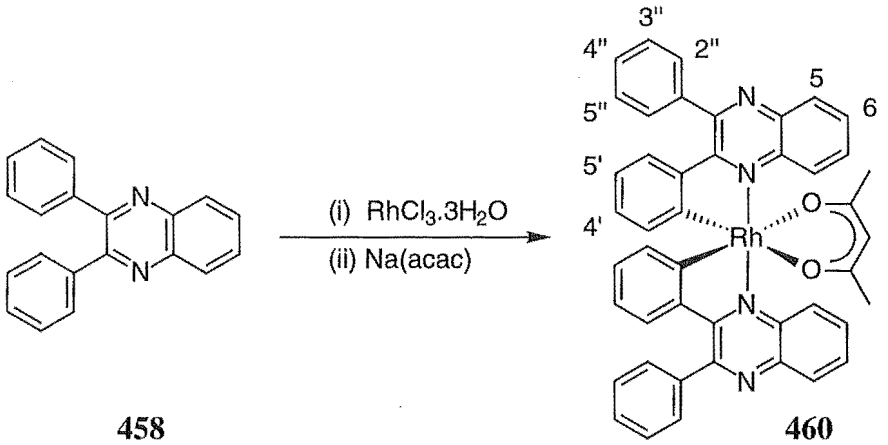
458



459

The reactions of two other potentially doubly cyclometallated ligands were examined in the course of this research. Both 2,3-diphenylquinoxaline (**458**) and dibenzo-[a,c]-phenazine (**459**), analogues of 2,3-diphenylpyrazine, **428** (*vide supra*), have previously been singly and doubly cyclopalladated.[111] Given the ease with which these cyclopalladation reactions take place, the reactions of these two ligands with rhodium trichloride were investigated.

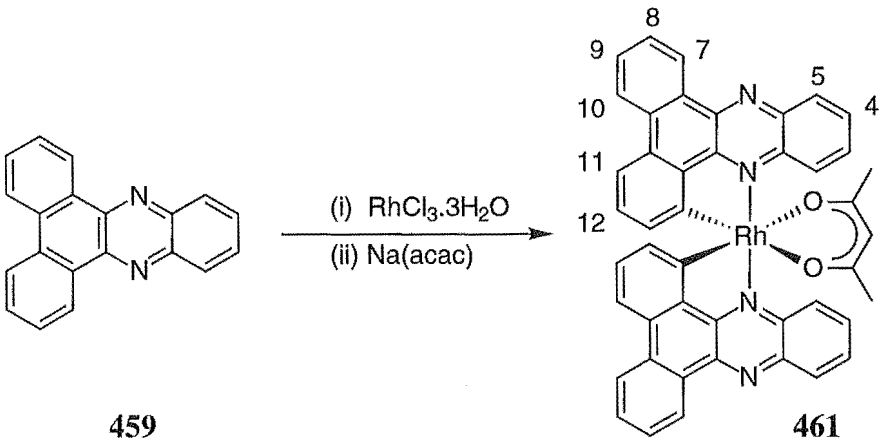
The ligands **458** and **459** and rhodium trichloride trihydrate were reacted with a rhodium:ligand ratio of one:two. Had the reactions been performed with a rhodium:ligand ratio of one:one, it is likely that a highly insoluble polymer would have resulted with rhodium atoms and ligands alternating to form an extended array.



Scheme 4.12

Reaction of **458** with rhodium trichloride in refluxing 2-methoxyethanol gave a chloro-bridged dimer, $[Rh(\mathbf{458}\text{-}H)_2Cl]_2$, as a yellow powder in good yield. This complex was smoothly converted to the mononuclear complex, $Rh(\mathbf{458}\text{-}H)_2(acac)$ (**460**), by a ligand exchange reaction with sodium acetylacetonate (scheme 4.12).

A similar reaction of **459** gave $[Rh(\mathbf{459}\text{-}H)_2Cl]_2$ as a reddish purple powder in quantitative yield. Ligand exchange with sodium acetylacetonate gave the corresponding mononuclear complex, $Rh(\mathbf{459}\text{-}H)_2(acac)$ (**461**) (scheme 4.13). Both of these monomeric cyclorhodated acetylacetonate complexes were characterised by FAB mass spectrometry and ^1H NMR spectroscopy (table 4.2), both complexes being insufficiently soluble in $CDCl_3$ to permit the acquisition of ^{13}C NMR spectra.



Scheme 4.13

Table 4.2 ^{1}H NMR of the free ligands (**458** and **459**) and cyclorhodated acetylacetonate complexes (**460** and **461**) (Δ = δ(complex)-δ(free ligand)).

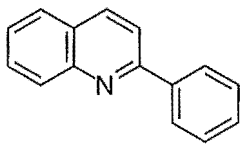
	H3'	*H4'*	*H5'*	*H6'*	*H2''*	*H3''*	*H4''*	*H5''*	*H6''*	*H5*	*H6*	*H7*	*H8*
458	7.35	7.35	7.35	7.53	7.53	7.35	7.35	7.35	7.53	8.19	7.79	7.79	8.19
460	6.52	6.60	6.67	7.08	8.00	7.61	7.61	7.61	8.00	8.12	7.69	7.55	8.48
Δ	**-0.83**	**-0.75**	**-0.68**	**-0.45**	**0.47**	**0.26**	**0.26**	**0.26**	**0.47**	**-0.07**	**-0.10**	**-0.24**	**0.29**
	H13	*H12*	*H11*		*H7*	*H8*	*H9*	*H10*		*H5*	*H4*	*H3*	*H2*
459	7.75	7.81	8.58		9.42	7.75	7.81	8.58		8.34	7.86	7.86	8.34
461	6.49	7.03	8.01		9.45	7.78	7.83	8.51		8.46	7.88	7.71	8.89
Δ	**-1.26**	**-0.78**	**-0.57**		**0.03**	**0.03**	**0.02**	**-0.07**		**0.12**	**0.02**	**-0.15**	**0.55**

It is interesting to compare the CIS values observed for the structurally equivalent protons in the ^{1}H NMR spectra of the two rhodium acetylacetonate complexes (table 4.2). The CIS values for both the proton adjacent to the metallated carbon (H-3' and H-13) and for the proton adjacent to the nitrogen donor (H-8 and H-2) is of greater magnitude for the phenazine complex than for the quinoxaline complex. Perhaps the most significant CIS differences, however, are those observed between the protons on the unmetallated phenyl ring (H-2''-H-6'') in **460** and the protons on the unmetallated benzo ring (H-7-H-10) in **461**. The CIS values for the former protons falls between 0.26 to 0.47 ppm whereas Δ for the latter protons range from -0.07 and 0.03 ppm upon cyclometallation.

This difference in the magnitude of the CIS values observed for these protons can be attributed to restrictions that cyclometallation places upon ligand conformation. Cyclometallation constrains the metallated carbon atom to lie approximately coplanar with the nitrogen donor atom. For complexes of **459** this coplanar geometry is already present by virtue of the fused structure of the ligand, therefore relatively minor changes occur in the ligand upon cyclometallation. In the case of **458**, cyclometallation considerably alters the ligand conformation as a freely rotating phenyl ring is restricted to a conformation that has it lying approximately coplanar with the quinoxaline system. The unmetallated phenyl ring will, for steric reasons, lie approximately orthogonal to

the plane of the other rings. This also accounts for the observed upfield shift of H-6' upon cyclometallation (Δ = -0.45 ppm) as it lies directly above the shielding plane of the unsubstituted phenyl ring, a similar shift being observed (Δ = -0.85 ppm) for the equivalent proton in the mono-palladated complex of this ligand.[111]

Attempts to prepare the corresponding rhodium benzoylacetonate and dibenzoylmethanate complexes by ligand exchange of the chloro-bridged dimers with the appropriate sodium ß-diketonate were unsuccessful. In all cases the only solid, if any, obtained from the attempted reactions was unreacted chloro-bridged dimer. Examination of molecular models suggests that unfavourable steric interactions between the phenyl rings on these ß-diketonate ligands and the benzo ring of the quinoxaline or phenazine prevent the formation of these monomeric rhodium ß-diketonate complexes.



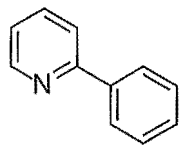
203

It is interesting to compare the product of the reaction of **458** and rhodium trichloride with the products of the reaction of its structural analogue, 2-phenylquinoline, **203**, under the same conditions. Upon reaction with two equivalents of rhodium trichloride trihydrate, **203** gives a mixture of two products which can be manually separated following diffusion of ether vapour into an acetonitrile solution of the mixture. This gives Rh(**203**-H)$_2$Cl.$^1/_4$CH$_3$CN, **204**, in which the ratio rhodium:ligand = one:two, and [Rh(**203**-H)(CH$_3$CN)Cl$_2$], **205**, in which the ratio rhodium:ligand = one:one (*vide supra*). In contrast, **458** gives only one product upon reaction with two equivalents of rhodium chloride, formulated as the chloro-bridged dimer, [Rh(**458**-H)$_2$Cl]$_2$, in which the ratio rhodium:ligand = one:two.

Given the structural similarity between **458** and **203** it is perhaps expected that the former would give a five-coordinate complex upon reaction with rhodium chloride, as is observed for reaction of the latter. However, without a single crystal X-ray

analysis, it is not possible to distinguish between a six-coordinate complex with a dimeric formulation, i.e. $[Rh(\mathbf{458}\text{-}H)_2Cl]_2$, and the five-coordinate monomeric equivalent, $Rh(\mathbf{458}\text{-}H)_2Cl$, which have the same stoichiometry. To this end, attempts were made to obtain crystals of the quinoxaline complex so that such an analysis might be performed. Unfortunately these attempts failed to give any suitable crystals and the precise nature of this complex remains unknown.

The monomeric rhodium acetylacetonate complexes are potential precursors to heterobimetallic complexes, as the potentially doubly cyclometallated ligands each have one free coordination site available. Such doubly cyclometallated complexes could be prepared by the reaction of the monomeric rhodium acetylacetonate complex with another metal ion, preferably one with square planar coordination geometry. Reaction with a metal ion with octahedral coordination geometry could lead to an insoluble polymer (*vide supra*).



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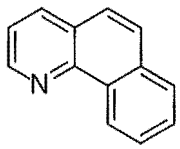


462

The complex $Rh(\mathbf{459}\text{-}H)_2(acac)$ was thought the most likely to give a doubly cyclometallated complex upon reaction with another metal ion, as the required coplanar geometry of nitrogen and carbon donors described above is already present—by virtue of the planarity of the fused dibenzo-[a,c]-phenazine ligand—in the starting complex. A similar reaction of $Rh(\mathbf{458}\text{-}H)_2(acac)$ would involve cyclometallation of a freely-rotating phenyl ring, a reaction that would be assumed to take place less readily. Unfortunately, all attempts to prepare a doubly cyclometallated complex by reaction of $Rh(\mathbf{459}\text{-}H)_2(acac)$ were unsuccessful.

CONCLUSION

This chapter has described the preparation and reactions of several new ligands which are potentially capable of bridging two metal ions *via* two cyclometallated sites. Limited success in the preparations of doubly cyclopalladated complexes has been reported utilising two novel ligands which are analogues of quaterpyridine. In addition, two ligands which have been previously cyclopalladated have been cyclorhodated and the resulting complexes characterised. Worthy of note are the preparations and cyclopalladations of the two diphenoxydiazines. These two ligands have both been cyclopalladated and the resultant complexes fully characterised including a single crystal X-ray structure determination of the cyclopalladated diphenoxypyridazine. This complex is a cyclometallated analogue of the phenoxypyridine coordination complex which is crystallographically characterised in Chapter Two.

Chapter Five

NMR Data Tabulation

and

Analysis

5.1 INTRODUCTION

Throughout the course of this work extensive use has been made of ^{1}H and ^{13}C NMR spectroscopy for the characterisation of both ligands and complexes. With NMR spectroscopy being a technique more commonly associated with organic chemistry, its application to ligand characterisation is not unusual. However the application of ^{1}H and ^{13}C NMR characterisation to metal complexes is somewhat less common, though becoming more frequent. Often the spectra reported in the literature are not fully assigned, their acquisition and assignment being of minor importance relative to the information gleaned from the more traditional inorganic techniques such as electrochemistry and IR and electronic spectroscopy. Also, single crystal X-ray diffraction data provides definitive structural information, though it must be remembered that this information applies to the solid state only; the conformations of the molecule in solution may be very different (possibly dynamic)—by way of example, consider the characterisation of the coordination complex, $Pd(2\text{-phenoxypyridine})_2Cl_2$, **234**, discussed in Chapter Two.

Despite their relatively infrequent use for cyclometallated and coordination complexes, different one- and two-dimensional homo- and hetero-nuclear NMR experiments usually permit the full assignment of both ^{1}H and ^{13}C spectra, these techniques having been illustrated by example in the preceding chapters. A complete review of the use of NMR spectroscopy for the characterisations of molecules of the type discussed in this work is beyond the scope of this chapter and the subject has been discussed elsewhere in the literature.[54,56,275]

In 1975 a paper was published by Todd and co-workers entitled "Application of ^{13}C NMR spectroscopy to the determination of metal-carbon σ bond formation in cyclometallation reactions with nitrogen donor ligands".[276] This detailed the use of single frequency off resonance decoupling experiments to establish the number of quaternary and C-H carbon atom resonances in the ^{13}C NMR spectrum of a given

cyclometallated complex, from which it could be established, given the numbers in the spectrum of the free ligand, whether or not cyclometallation had occurred.

Twelve years later, Steel and Caygill published definitively assigned ^{1}H and ^{13}C NMR spectra of nineteen cyclopalladated acetylacetonate complexes together with a statistical analysis of the CIS data for the phenyl ring of the cyclopalladated ligand.[54] This study showed that the Pd(acac) substituent leads to characteristic CIS values in both the ^{1}H and ^{13}C NMR spectra. This paper has been frequently cited since, despite criticism from other authors that no mention is made of the chemical shift of the quaternary deprotonated aromatic carbons, including that directly joined to the metal—which should show the greatest CIS upon cyclopalladation.[277,278]

In the same year, Arz *et al.* published a study of a variety of rhodium(III) complexes which contain two cyclometallated Schiff base ligands.[279] This paper included—in addition to the ^{1}H chemical shifts of the coordinated hydride and the ^{31}P NMR shifts of the ancillary triphenylphosphine ligands—^{103}Rh NMR spectral data, and was directed toward developing systematic chemical shift-structure correlations. The ^{1}H and ^{13}C NMR chemical shifts of the cyclometallated ligands were not included.

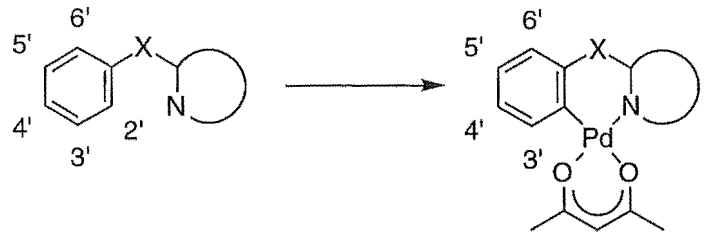
In 1986, von Zelewsky and co-workers published the preparation and ^{1}H NMR spectrum of $[Rh(\mathbf{201})_2(bipy)]^+$, a mononuclear complex obtained from the chloro-bridged dimer, $[Rh(\mathbf{201})_2Cl]_2$.[102] This report was followed, six years later, by another which detailed the preparation and ^{1}H NMR spectra of a number of analogous complexes—with the general formula, $[Rh(C\text{-}N)_2(N\text{-}N)]^+$—incorporating a variety of cyclorhodated (C-N) and diimine (N-N) ligands.[107] Whilst these two papers included fully assigned ^{1}H NMR spectra of the complexes, no discussion of the CIS values was included; indeed these could not even be calculated due to the absence of ^{1}H NMR spectral data for the free ligands.

Garces and Watts published "^{1}H and ^{13}C NMR Assignments with Coordination-Induced Shift Calculations of Carbon σ-Bonded *Ortho*-Metalated Rhodium(III) and Iridium(III) Complexes", in 1993.[109] This was the first paper to address the concept of

CIS calculations as they apply to rhodium(III) and iridium(III) cyclometallated complexes. However, the two rhodium complexes considered—$[Rh(\mathbf{201})_2Cl]_2$ and $[Rh(\mathbf{201})_2(bipy)]^+$—had previously been studied. The authors used the obtained CIS data to provide "insight into how σ-donation and π-back-bonding affect the electronic environment of the H and C sites in the *ortho*-metalated complexes."[109]

It is apparent, therefore, that there is a dearth of definitive assignments for the spectra of cyclorhodated complexes and there are no corresponding theoretical or empirical rules to predict the ^1H and ^{13}C NMR CIS values that cyclometallation by rhodium(III) might effect. Having prepared, during the course of this research, a series of cyclometallated rhodium ß-diketonate complexes and assigned their ^1H and ^{13}C NMR spectra—all of which were acquired under identical conditions—this chapter discusses the CIS values found for such complexes. Also the results of a statistical analysis of these data for the cyclorhodated phenyl ring—a structural element common to all of the complexes—are presented. Given that ten years have passed since the publication of Steel and Caygill's analysis of cyclopalladated acetylacetonate complexes (*vide supra*), a timely updating of their results to include data published subsequently, in addition to those obtained in the course of this research, is also presented.

5.2 CYCLOPALLADATED COMPLEXES: ^1H AND ^{13}C NMR DATA TABULATION AND ANALYSIS



LH **PdL(acac)**

Figure 5.1 Numbering scheme used for the free ligands (LH) and palladium acetylacetonate complexes (PdL(acac)) where X represents the presence (six-membered palladacycle) or absence (five-membered palladacycle) of a spacer group.

Table 5.1 ^{1}H NMR chemical shifts of the phenyl ring for the free ligands and palladium acetylacetonate complexes where Δ = CIS = δ(complex(ppm)) - δ(free ligand(ppm)).

	H-3'	*H-4'*	*H-5'*	*H-6'*	*Reference*
Acyclic Nitrogen Donor Complexes (Five-membered palladacycles)					
LH=*E*-acetophenone oxime	7.38	7.38	7.38	7.62	54
PdL(acac)	7.42	7.13	7.06	7.10	54
Δ	**0.04**	**-0.25**	**-0.32**	**-0.52**	
LH=*N*-benzylideneaniline	7.47	7.47	7.47	7.90	54
PdL(acac)	7.62	7.23	7.10	7.39	54
Δ	**0.15**	**-0.24**	**-0.37**	**-0.51**	
LH=*N*-(4-methoxyphenyl)-α-benzoylbenzylidene amine	7.31	7.42	7.31	7.75	278
PdL(acac)	7.69	7.25	7.00	7.00	278
Δ	**0.38**	**-0.17**	**-0.31**	**-0.75**	
LH=*N*-benzylidenebenzylamine	7.41	7.41	7.41	7.78	54
PdL(acac) (endo-cyclic imine)	7.51	7.20	7.02	7.21	54
Δ	**0.10**	**-0.21**	**-0.39**	**-0.57**	
LH=*N*-benzylidenebenzylamine	7.34	7.27	7.34	7.34	54
PdL(acac) (exo-cyclic imine)	7.40	7.06	7.06	6.98	54
Δ	**0.06**	**-0.21**	**-0.28**	**-0.36**	
LH=azobenzene	7.49	7.44	7.49	7.92	54
PdL(acac)	7.60	7.28	7.26	7.93	54
Δ	**0.11**	**-0.16**	**-0.23**	**0.01**	
LH=azoxybenzene	7.51	7.56	7.51	8.32	54
PdL(acac)	7.73	7.42	7.22	7.59	54
Δ	**0.22**	**-0.14**	**-0.29**	**-0.73**	
***N*-Heterocyclic Donor Complexes** (Five-membered palladacycles)					
LH=1-phenylpyrazole (**116**)	7.44	7.27	7.44	7.69	54,89
PdL(acac)	7.55	7.07	7.12	7.06	54,89
Δ	**0.11**	**-0.20**	**-0.32**	**-0.63**	
LH=3,5-dimethylpyrazole	7.43	7.33	7.43	7.43	54,89
PdL(acac)	7.60	7.01	7.08	7.13	54,89
Δ	**0.17**	**-0.32**	**-0.35**	**-0.30**	
LH=3-phenyl-1-methylpyrazole	7.30	7.30	7.30	7.81	280
PdL(acac)	7.50	7.05	7.05	7.23	280
Δ	**0.20**	**-0.25**	**-0.25**	**-0.58**	

	H-3'	*H-4'*	*H-5'*	*H-6'*	*Reference*
LH=1,5-diphenyl-3-methylpyrazole	7.28	7.25	7.28	7.27	54,89
PdL(acac)	7.55	6.93	6.74	6.34	54,89
Δ	**0.27**	**-0.32**	**-0.54**	**-0.93**	
LH=3,5-diphenyl-1-methylpyrazole	7.40	7.40	7.40	7.83	280
PdL(acac)	7.53	7.06	7.06	7.24	280
Δ	**0.13**	**-0.34**	**-0.34**	**-0.59**	
LH=1,3,5-triphenylpyrazole	7.31	7.28	7.31	7.35	54,89
PdL(acac)	7.57	6.96	6.76	6.39	54,89
Δ	**0.26**	**-0.32**	**-0.55**	**-0.96**	
LH_2=bis(3-phenyl-1-pyrazolyl)methane	7.38	7.38	7.38	7.80	281
$L[Pd(acac)]_2$	7.30	7.00	7.45	7.00	281
Δ	**-0.08**	**-0.38**	**0.07**	**-0.80**	
LH_2=(3-phenyl-1-pyrazolyl)(5-phenyl-1-pyrazolyl)methane	7.51	7.51	7.51	7.51	281
$L[Pd(acac)]_2$	7.31	7.05	7.50	7.05	281
Δ	**-0.20**	**-0.46**	**-0.01**	**-0.46**	
LH=2-phenylimidazoline (**101**)	7.35	7.41	7.35	7.77	
PdL(acac) (**105**)	7.57	7.18	7.01	7.01	
Δ	**0.22**	**-0.23**	**-0.34**	**-0.76**	
LH=2-phenylthiazole (**115**)	7.45	7.45	7.45	7.95	54
PdL(acac)	7.58	7.17	7.09	7.36	54
Δ	**0.13**	**-0.28**	**-0.36**	**-0.59**	
LH=2-phenylbenzoxazole (**121**)	7.53	7.53	7.53	8.26	54
PdL(acac)	7.65	7.27	7.15	7.54	54
Δ	**0.12**	**-0.26**	**-0.38**	**-0.72**	
LH=2-phenylbenzothiazole (**126**)	7.49	7.49	7.49	8.10	54
PdL(acac)	7.65	7.21	7.13	7.44	54
Δ	**0.16**	**-0.28**	**-0.36**	**-0.66**	
LH=2-phenyl-1,2,3-triazole (**127**)	7.48	7.35	7.48	8.09	54
PdL(acac)	7.58	7.18	7.21	7.52	54
Δ	**0.10**	**-0.17**	**-0.27**	**-0.57**	
LH=2-phenylpyridine (**201**)	7.46	7.39	7.46	7.98	54
PdL(acac)	7.60	7.17	7.11	7.42	54
Δ	**0.14**	**-0.22**	**-0.35**	**-0.56**	
LH=2-phenyl-6-(2-thienyl)pyridine	7.47	7.50	7.47	8.12	30e
PdL(acac)	7.52	7.14	7.14	7.52	30e
Δ	**0.05**	**-0.36**	**-0.33**	**-0.60**	

	H-3'	*H-4'*	*H-5'*	*H-6'*	*Reference*
LH=2,2'-diphenyl-4,4'-bipyridine (**402**)	7.51	7.45	7.51	8.06	
PdL(acac) (**413**)	7.63	7.22	7.15	7.52	
Δ	**0.12**	**-0.23**	**-0.36**	**-0.54**	
LH=2-phenylquinoline (**203**)	7.49	7.44	7.49	8.16	111
PdL(acac)	7.69	7.19	7.14	7.52	111
Δ	**0.20**	**-0.25**	**-0.35**	**-0.64**	
LH=benzo[*h*]quinoline (**462**)	7.74	7.68	7.89		54
PdL(acac)	7.70	7.51	7.56		54
Δ	**-0.04**	**-0.17**	**-0.33**		
LH=3,2'-trimethylene-2-phenylpyridine	Not listed	7.34	7.23		282
PdL(acac)	6.89	7.02	7.56		282
Δ	—	**-0.32**	**0.33**		
LH=4-phenylpyrimidine (**202**)	7.52	7.52	7.52	8.09	110
PdL(acac)	7.63	7.26	7.14	7.50	110
Δ	**0.11**	**-0.26**	**-0.38**	**-0.59**	
LH=4-methyl-6-phenylpyrimidine	7.50	7.50	7.50	8.07	110
PdL(acac)	7.62	7.25	7.13	7.50	110
Δ	**0.12**	**-0.25**	**-0.37**	**-0.57**	
LH=4,6-diphenylpyrimidine (**209**)	7.54	7.54	7.54	8.15	110
PdL(acac)	7.65	7.27	7.16	7.62	110
Δ	**0.11**	**-0.27**	**-0.38**	**-0.53**	
LH=4-(*para*-nitrophenyl)-6-phenylpyrimidine	7.57	7.57	7.57	8.18	110
PdL(acac)	7.67	7.31	7.19	7.64	110
Δ	**0.10**	**-0.26**	**-0.38**	**-0.54**	
LH=4,6-dimethyl-2-phenylpyrimidine	7.46	7.46	7.46	8.43	110
PdL(acac)	7.61	7.20	7.12	7.81	110
Δ	**0.15**	**-0.26**	**-0.34**	**-0.62**	
LH=2,4-diphenyl-6-methylpyrimidine	7.50	7.50	7.50	8.58	110
PdL(acac)	7.65	7.24	7.17	7.99	110
Δ	**0.15**	**-0.26**	**-0.33**	**-0.59**	
LH=2,4,6-triphenylpyrimidine	7.53	7.53	7.53	8.73	110
PdL(acac) (2-phenyl ring metallated)	7.65	7.28	7.22	8.06	110
Δ	**0.12**	**-0.25**	**-0.31**	**-0.67**	
LH=2,4,6-triphenylpyrimidine	7.53	7.53	7.53	8.29	110
PdL(acac) (4-phenyl ring metallated)	7.67	7.28	7.21	7.70	110
Δ	**0.14**	**-0.25**	**-0.32**	**-0.59**	

	H-3'	*H-4'*	*H-5'*	*H-6'*	*Reference*
LH=2,3-diphenylpyrazine (**458**)	7.30	7.30	7.30	7.45	111
PdL(acac)	7.62	7.10	6.75	6.64	111
Δ	**0.32**	**-0.20**	**-0.55**	**-0.81**	
LH=2,3-dihydro-5,6-diphenylpyrazine	7.24	7.30	7.24	7.40	111
PdL(acac)	7.60	7.13	6.74	6.45	111
Δ	**0.36**	**-0.17**	**-0.50**	**-0.95**	
LH=dibenzo[*f*,*h*]quinoxaline	7.68	7.73	8.53		111
PdL(acac)	7.67	7.56	8.14		111
Δ	**-0.01**	**-0.17**	**-0.39**		
LH=2,3-diphenylquinoxaline (**458**)	7.34	7.34	7.34	7.53	111
PdL(acac)	7.69	7.08	6.76	6.68	111
Δ	**0.35**	**-0.26**	**-0.58**	**-0.85**	
LH=dibenzo[*a*,*c*]phenazine (**459**)	7.72	7.77	8.52		111
PdL(acac)	7.56	7.37	7.56		111
Δ	**-0.16**	**-0.40**	**-0.56**		
***N*-Heterocyclic Donor Complexes** (Six-membered palladacycles)					
LH=1-benzylpyrazole	7.33	7.30	7.33	7.20	54,89
PdL(acac)	7.52	7.10	7.00	6.96	54,89
Δ	**0.19**	**-0.20**	**-0.30**	**-0.24**	
LH=1-benzoylpyridine (**301**)	7.47	7.58	7.47	8.06	54
PdL(acac)	7.81	7.52	7.19	7.77	54
Δ	**0.34**	**-0.26**	**-0.28**	**-0.29**	
LH=2-phenoxypyridine (**232**)	7.40	7.20	7.40	7.14	
PdL(acac) (**237**)	7.62	7.06	7.12	6.98	
Δ	**0.22**	**-0.14**	**-0.28**	**-0.16**	
LH=2-phenylthiopyridine (**233**)	7.41	7.41	7.41	7.59	
PdL(acac) (**239**)	7.44	7.07	7.01	7.30	
Δ	**0.03**	**-0.34**	**-0.30**	**-0.29**	
LH=3,6-diphenoxypyridazine (**419**)	7.36	7.17	7.36	7.18	
PdL(acac) (**455**)	7.60	7.10	7.07	6.96	
Δ	**0.24**	**-0.07**	**-0.29**	**-0.22**	
LH=4,6-diphenoxypyrimidine (**420**)	7.44	7.28	7.44	7.16	
PdL(acac) (**454**)	7.65	7.10	7.10	6.94	
Δ	**0.21**	**-0.18**	**-0.34**	**-0.22**	

Table 5.2 Results of a statistical analysis of the data in table 5.1, the ^{1}H NMR chemical shifts of the phenyl ring of the free ligands and palladium acetylacetonate complexes.

	H-3'	*H-4'*	*H-5'*	*H-6'*
# ACYCLIC NITROGEN DONOR COMPLEXES (Five-membered palladacycles)	7	7	7	7
Mean CIS (ppm)	+0.15	-0.20	-0.31	-0.49
Standard deviation	0.11	0.04	0.05	0.24
# *N*-HETEROCYCLIC DONOR COMPLEXES (Five-membered palladacycles)	31	32	32	28
Mean CIS (ppm)	+0.13	-0.27	-0.34	-0.65
Standard deviation	0.12	0.07	0.18	0.15
# *N*-HETEROCYCLIC DONOR COMPLEXES (Six-membered palladacycles)	6	6	6	6
Mean CIS (ppm)	+0.21	-0.20	-0.30	-0.24
Standard deviation	0.09	0.09	0.02	0.05
# *N*-HETEROCYCLIC DONOR COMPLEXES (Five- and six-membered palladacycles)	37	38	38	34
Mean CIS (ppm)	+0.14	-0.26	-0.33	-0.58
Standard deviation	0.12	0.08	0.16	0.21
# ALL NITROGEN DONOR COMPLEXES (Five- and six-membered palladacycles)	44	45	45	41
Mean CIS (ppm)	+0.14	-0.25	-0.33	-0.56
Standard deviation	0.12	0.07	0.15	0.22

Table 5.3 ^{13}C NMR chemical shifts of the phenyl ring for the free ligands and palladium acetylacetonate complexes where Δ = CIS = δ(complex(ppm)) - δ(free ligand(ppm)).

	C-3'	*C4'*	*C-5'*	*C-6'*	*Reference*
Acyclic Nitrogen Donor Complexes (Five-membered palladacycles)					
LH=*E*-acetophenone oxime	128.5	129.3	128.5	126.1	54
PdL(acac)	130.4	128.6	124.5	124.6	54
Δ	**1.9**	**-0.7**	**-4.0**	**-1.5**	
LH=*N*-benzylideneaniline	128.8	131.4	128.8	128.8	54
PdL(acac)	130.9	130.5	124.6	127.9	54
Δ	**2.1**	**-0.9**	**-4.2**	**-0.9**	
LH=*N*-(4-methoxyphenyl)-α-benzoylbenzylidene amine	129.2	131.3	129.2	128.8	278
PdL(acac)	131.4	131.0	124.4	128.0	278
Δ	**2.2**	**-0.3**	**-4.8**	**-0.8**	
LH=*N*-benzylidenebenzylamine	128.6	130.7	128.6	128.3	54
PdL(acac) (endo-cyclic imine)	130.9	129.8	124.2	126.8	54
Δ	**2.3**	**-0.9**	**-4.4**	**-1.5**	
LH=*N*-benzylidenebenzylamine	128.5	127.0	128.5	128.0	54
PdL(acac) (exo-cyclic imine)	130.6	125.1	124.7	119.8	54
Δ	**2.1**	**-1.9**	**-3.8**	**-8.2**	
LH=azobenzene	129.1	131.0	129.1	122.9	54
PdL(acac)	131.5	131.2	125.7	128.8	54
Δ	**2.4**	**0.2**	**-3.4**	**5.9**	
LH=azoxybenzene	128.8	131.6	128.8	122.4	54
PdL(acac)	130.7	132.7	125.3	121.5	54
Δ	**1.9**	**1.1**	**-3.5**	**-0.9**	
***N*-Heterocyclic Donor Complexes** (Five-membered palladacycles)					
LH=1-phenylpyrazole (**116**)	129.4	126.4	129.4	119.2	54,89
PdL(acac)	132.0	125.1	124.9	110.5	54,89
Δ	**2.6**	**-1.3**	**-4.5**	**-8.7**	
LH=3,5-dimethylpyrazole	128.9	127.2	128.9	124.7	54,89
PdL(acac)	131.5	123.8	124.8	111.5	54,89
Δ	**2.6**	**-3.4**	**-4.1**	**-13.2**	
LH=1,5-diphenyl-3-methylpyrazole	128.8	127.0	128.8	125.1	54,89
PdL(acac)	131.2	124.0	124.3	112.7	54,89
Δ	**2.4**	**-3.0**	**-4.5**	**-12.4**	

	C-3'	*C4'*	*C-5'*	*C-6'*	*Reference*
LH=1,3,5-triphenylpyrazole	128.9	127.4	128.9	125.3	54,89
PdL(acac)	131.4	124.5	124.3	113.4	54,89
Δ	**2.5**	**-2.9**	**-4.6**	**-11.9**	
LH=2-phenylimidazoline (**101**)	128.2	130.4	128.2	126.8	
PdL(acac) (**105**)	131.0	129.8	123.3	123.6	
Δ	**2.8**	**-0.6**	**-4.9**	**-3.2**	
LH=2-phenylthiazole (**115**)	129.1	130.4	129.1	126.8	54
PdL(acac)	131.1	129.0	124.7	122.9	54
Δ	**2.0**	**-1.4**	**-4.4**	**-3.9**	
LH=2-phenylbenzoxazole (**121**)	128.9	131.5	128.9	127.6	54
PdL(acac)	130.9	131.0	124.8	124.4	54
Δ	**2.0**	**-0.5**	**-4.1**	**-3.2**	
LH=2-phenylbenzothiazole (**126**)	129.0	131.0	129.0	127.6	54
PdL(acac)	130.9	130.6	124.9	124.4	54
Δ	**1.9**	**-0.4**	**-4.1**	**-3.2**	
LH=2-phenyl-1,2,3-triazole (**127**)	129.3	127.5	129.3	118.9	54
PdL(acac)	131.4	126.8	125.5	113.6	54
Δ	**2.1**	**-1.3**	**-3.8**	**-5.3**	
LH=2-phenylpyridine (**201**)	128.6	128.8	128.6	126.8	54
PdL(acac)	131.4	129.1	124.6	122.8	54
Δ	**2.8**	**0.2**	**-4.0**	**-4.0**	
LH=2,2'-diphenyl-4,4'-bipyridine (**402**)	128.8	129.3	128.8	127.0	
PdL(acac) (**413**)	131.5	129.5	124.7	123.0	
Δ	**2.7**	**0.2**	**-4.1**	**-4.0**	
LH=2-phenylquinoline (**203**)	128.8	129.3	128.8	127.5	111
PdL(acac)	130.7	129.0	124.8	124.4	111
Δ	**1.9**	**-0.3**	**-4.0**	**-3.1**	
LH=benzo[*h*]quinoline (**462**)	127.1	128.2	127.8		54
PdL(acac)	128.9	122.4	122.8		54
Δ	**1.8**	**-5.8**	**-5.0**		
LH=4-phenylpyrimidine (**202**)	129.0	131.0	129.0	127.1	110
PdL(acac)	131.8	131.2	124.9	124.5	110
Δ	**2.8**	**0.2**	**-4.1**	**-2.6**	
LH=4-methyl-6-phenylpyrimidine	128.8	130.7	128.8	127.0	110
PdL(acac)	131.6	130.7	124.6	123.9	110
Δ	**2.8**	**0.0**	**-4.2**	**-3.1**	
LH=4,6-diphenylpyrimidine (**209**)	128.9	130.8	128.9	127.1	110
PdL(acac)	131.8	130.9	124.7	124.1	110
Δ	**2.9**	**0.1**	**-4.2**	**-3.0**	

	C-3'	*C4'*	*C-5'*	*C-6'*	*Reference*
LH=4-(*para*-nitrophenyl)-6-phenylpyrimidine	129.2	131.4	129.2	127.3	110
PdL(acac)	132.0	131.6	125.0	124.5	110
Δ	**2.8**	**0.2**	**-4.2**	**-2.8**	
LH=4,6-dimethyl-2-phenylpyrimidine	128.3	130.1	128.3	128.1	110
PdL(acac)	129.6	130.0	124.9	126.7	110
Δ	**1.3**	**-0.1**	**-3.4**	**-1.4**	
LH=2,4-diphenyl-6-methylpyrimidine	128.3	130.4	128.3	128.2	110
PdL(acac)	129.5	130.0	124.8	126.8	110
Δ	**1.2**	**-0.4**	**-3.5**	**-1.4**	
LH=2,4,6-triphenylpyrimidine	128.4	130.5	128.4	128.3	110
PdL(acac) (2-phenyl ring metallated)	129.9	130.1	124.8	126.9	110
Δ	**1.5**	**-0.4**	**-3.6**	**-1.4**	
LH=2,4,6-triphenylpyrimidine	128.8	130.7	128.8	127.2	110
PdL(acac) (4-phenyl ring metallated)	129.9	130.2	124.7	124.0	110
Δ	**1.1**	**-0.5**	**-4.1**	**-3.2**	
LH=2,3-diphenylpyrazine (**428**)	128.6	129.6	128.6	128.2	111
PdL(acac)	131.2	129.5	124.2	127.3	111
Δ	**2.6**	**-0.1**	**-4.4**	**-0.9**	
LH=2,3-dihydro-5,6-diphenylpyrazine	128.1	129.6	128.1	127.8	111
PdL(acac)	131.3	130.2	123.5	128.9	111
Δ	**3.2**	**0.6**	**-4.6**	**1.1**	
LH=dibenzo[*f*,*h*]quinoxaline	127.6	129.5	122.6		111
PdL(acac)	130.3	129.7	118.2		111
Δ	**2.7**	**0.2**	**-4.4**		
LH=2,3-diphenylquinoxaline (**458**)	128.2	128.8	128.2	129.8	111
PdL(acac)	130.7	129.0	124.3	129.0	111
Δ	**2.5**	**0.2**	**-3.9**	**-0.8**	
***N*-Heterocyclic Donor Complexes** (Six-membered palladacycles)					
LH=1-benzylpyrazole	128.8	128.0	128.8	127.6	54,89
PdL(acac)	134.2	126.8	124.2	125.1	54,89
Δ	**5.4**	**-1.2**	**-4.6**	**-2.5**	
LH=1-benzoylpyridine (**301**)	128.1	132.9	128.1	130.9	54
PdL(acac)	128.4	131.1	125.0	134.2	54
Δ	**0.3**	**-1.8**	**-3.1**	**3.3**	
LH=2-phenoxypyridine (**232**)	129.7	124.6	129.7	121.1	
PdL(acac) (**237**)	133.8	123.7	125.7	115.4	
Δ	**4.1**	**-0.9**	**-4.0**	**-5.7**	

	C-3'	*C4'*	*C-5'*	*C-6'*	*Reference*
LH=2-phenylthiopyridine (**233**)	129.5	129.0	129.5	134.8	
PdL(acac) (**239**)	135.8	126.0	124.6	126.8	
Δ	**6.3**	**-3.0**	**-4.9**	**-8.0**	
LH=3,6-diphenoxypyridazine (**419**)	129.6	125.0	129.6	121.0	
PdL(acac) (**455**)	134.3	125.5	124.3	115.1	
Δ	**4.7**	**0.5**	**-5.3**	**-5.9**	
LH=4,6-diphenoxypyrimidine (**420**)	129.9	125.9	129.9	121.5	
PdL(acac) (**454**)	133.7	124.3	126.5	115.5	
Δ	**3.8**	**-1.6**	**-3.4**	**-6.0**	

Table 5.4 Results of a statistical analysis of the data in table 5.3, the ^{13}C NMR chemical shifts of the phenyl ring of the free ligands and palladium acetylacetonate complexes.

	C-3'	*C-4'*	*C-5'*	*C-6'*
# ACYCLIC NITROGEN DONOR COMPLEXES (Five-membered palladacycles)	7	7	7	7
Mean CIS (ppm)	+2.1	-0.5	-4.0	-1.1
Standard deviation	0.2	0.9	0.5	4.1
# *N*-HETEROCYCLIC DONOR COMPLEXES (Five-membered palladacycles)	25	25	25	23
Mean CIS (ppm)	+2.3	-0.8	-4.2	-4.2
Standard deviation	0.6	1.5	0.4	3.7
# *N*-HETEROCYCLIC DONOR COMPLEXES (Six-membered palladacycles)	6	6	6	6
Mean CIS (ppm)	+4.1	-1.3	-4.2	-4.1
Standard deviation	1.9	1.1	0.8	3.7
# *N*-HETEROCYCLIC DONOR COMPLEXES (Five- and six-membered palladacycles)	31	31	31	29
Mean CIS (ppm)	+2.6	-0.9	-4.2	-4.2
Standard deviation	1.2	1.4	0.5	3.7

	C-3'	*C-4'*	*C-5'*	*C-6'*
# ALL NITROGEN DONOR COMPLEXES (Five- and six-membered palladacycles)	38	38	38	36
Mean CIS (ppm)	+2.6	-0.8	-4.2	-3.6
Standard deviation	1.1	1.3	0.5	3.9

Tables 5.1 and 5.3 list the assigned ^{1}H and ^{13}C NMR chemical shifts respectively for the ligand LH and PdL(acac) complex, along with the CIS = Δ = δ(complex) - δ(free ligand). Note that the spectra are grouped together according to the type of nitrogen donor and the size of the resultant metallocycle. In addition tables 5.2 and 5.4 list the results of statistical analyses of the data from tables 5.1 and 5.3 respectively, with the data for each of the three classes of complex analysed separately and in two groups, namely: (i) all *N*-heterocyclic donor PdL(acac) complexes; and (ii) all PdL(acac) complexes.

Consideration of the CIS values observed in the NMR spectra of the cyclopalladated complexes shows that some consistent patterns exist. Figures 5.2 and 5.3 show a graphical representation of the data in tables 5.1 and 5.3 and illustrate more clearly the consistent patterns as the calculated standard deviations for the mean CIS values are somewhat exaggerated, due to the presence in each data set of several outlying data points. The two figures demonstrate that the most reliable signals for predicting the chemical shifts of the cyclopalladated phenyl ring, based on the CIS of signals in the spectra of the ligands, are those for H-4' and C-5'.

Protons H-3' and the carbons to which they are attached (C-3') show a small—but consistent—downfield shift, the magnitude of which is significantly greater for those ligands which form a six-membered metallocycle. In the square planar palladium acetylacetonate complexes, these two atoms are influenced by the deshielding effect of

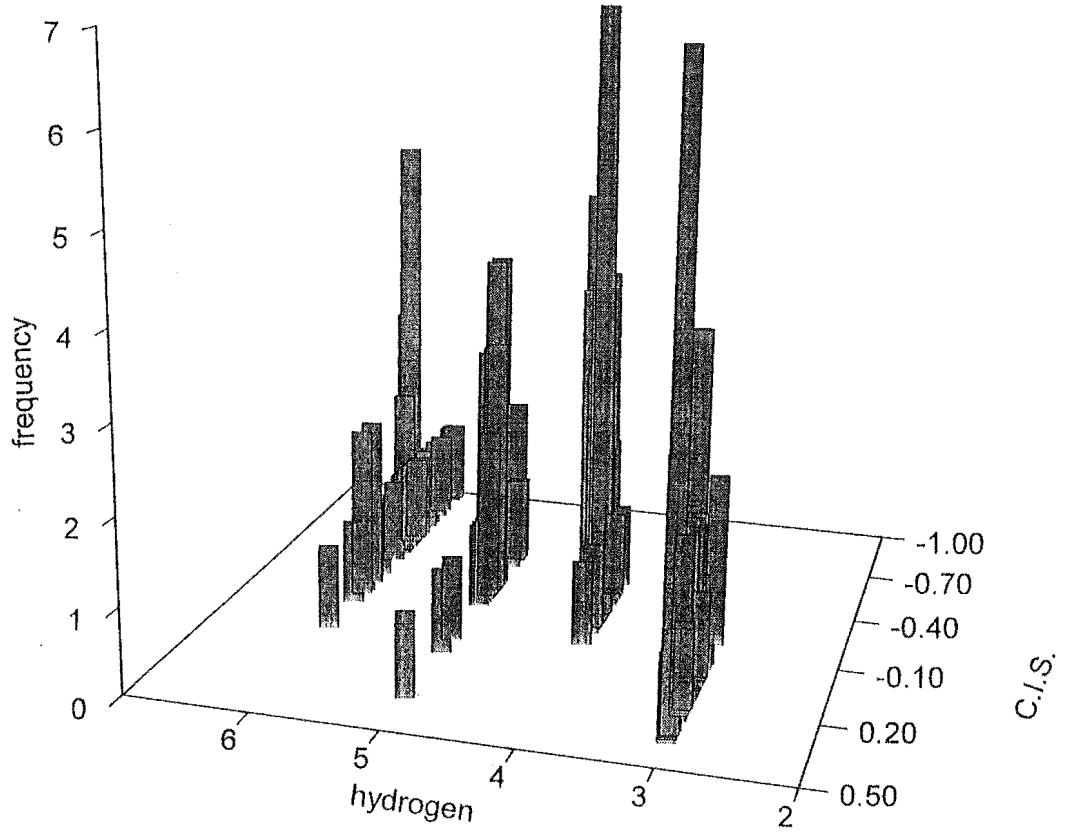


Figure 5.2 Plot of frequency versus CIS for the ^{1}H NMR chemical shifts of the phenyl ring in cyclometallated palladium acetylacetonate complexes.

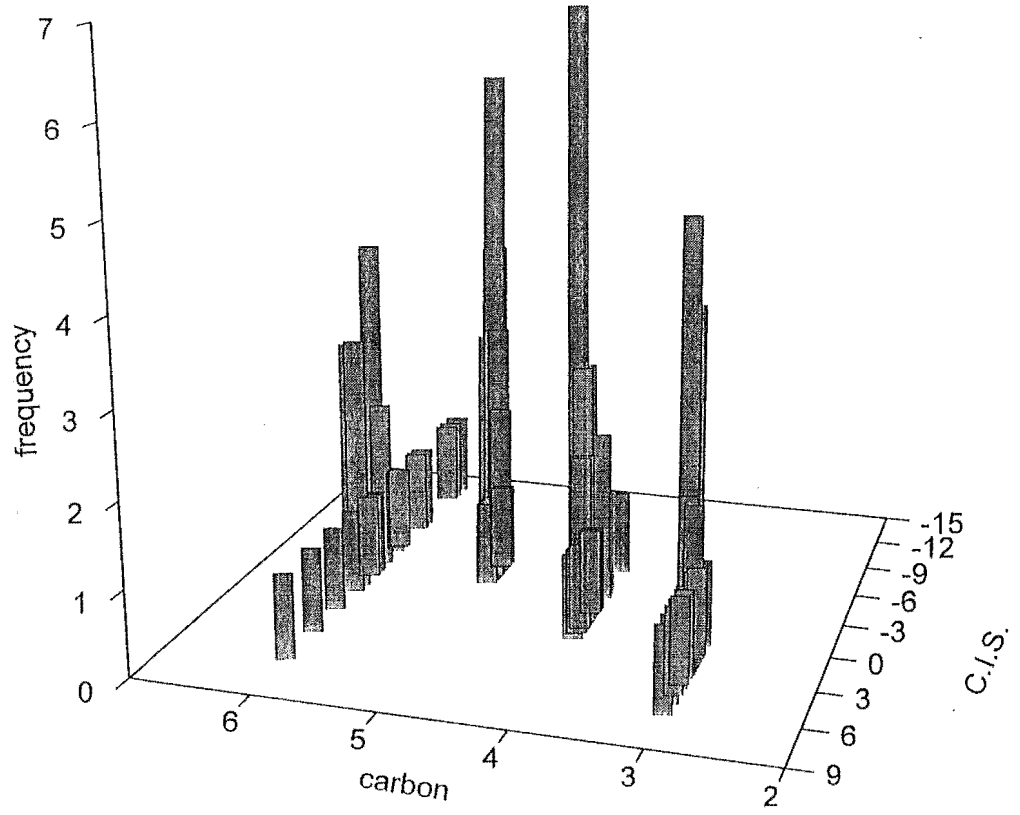


Figure 5.3 Plot of frequency versus CIS for the ^{13}C NMR chemical shifts of the phenyl ring in cyclometallated palladium acetylacetonate complexes.

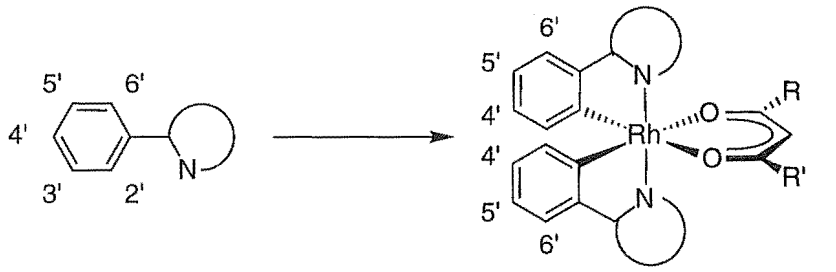
the lone pair on the oxygen atom of the acac ligand. Comparing the proximity of C-3' and H-3' to this lone pair for a complex with a five-membered palladacycle, relative to that with a six-membered palladacycle, provides an explanation for the difference in magnitude of this downfield shift in the two systems. 1-Phenylpyrazole forms a five-membered metallocycle (A, figure 5.4) upon cyclopalladation, whilst 1-benzylpyrazole forms a six-membered metallocycle (B, figure 5.4). As can be seen in figure 5.4, the geometry of the six-membered metallocycle (B) is such that C-3' and H-3' must lie closer to the oxygen atom of the acac ligand in this structure, than in that which contains the five-membered metallocycle (A). Thus 1-phenylpyrazole has CIS values of 0.11 ppm and 2.6 ppm for H-3' and C-3' respectively, whilst 1-benzylpyrazole has CIS values of greater magnitude, 0.19 ppm and 5.4 ppm, for the corresponding positions.

A **B**

Figure 5.4

C-5', which is *para* to the palladium atom and unaffected by steric interactions, exhibits a consistent, and relatively large, upfield shift and this has been attributed to the existence of some metal-to-ligand back-bonding.[54] Protons H-6' and carbons C-6' show inconsistent CIS values of often relatively large magnitude and this can be attributed to the cyclometallation-induced conformational changes which occur within the ligand.[54] For example, in the case of a ligand in which two rings are constrained to be coplanar in a cyclopalladated complex, but not in the free ligand, a large upfield shift may be observed for H-6' and C-6'.[54] H-6' may be less affected by such conformational changes in the case of a ligand which forms a six-membered palladacycle hence the observed CIS for this atom are more consistent and of relatively lesser magnitude.

5.3 CYCLORHODATED COMPLEXES: ^{1}H AND ^{13}C NMR DATA TABULATION AND ANALYSIS



LH

RhL_2(acac) R=R'=CH_3
RhL_2(dbm) R=R'=C_6H_5
RhL_2(bac) R=CH_3, R'=C_6H_5

Figure 5.4 Numbering scheme used for free ligands (LH) and rhodium acetylacetonate (RhL_2(acac)), dibenzoylmethanate (RhL_2(dbm)) and benzoylacetonate (RhL_2(bac)) complexes (note that analogous numbering is employed for the ^{1}H NMR spectra of the chloro-bridged dimers, $[RhL_2Cl]_2$).

Table 5.5 ^{1}H NMR chemical shifts of the phenyl ring for the free ligands and cyclorhodated complexes where Δ = CIS = δ(complex(ppm)) - δ(free ligand(ppm)).

	H-3'	*H-4'*	*H-5'*	*H-6'*	*Reference*
LH=1-phenylpyrazole (**116**)	7.44	7.27	7.44	7.69	96
$[RhL_2Cl]_2$	6.01	6.60	6.84	7.12	96
Δ	**-1.43**	**-0.67**	**-0.60**	**-0.57**	
RhL_2(acac)	6.22	6.70	6.88	7.13	96
Δ	**-1.22**	**-0.57**	**-0.56**	**-0.56**	
RhL_2(dbm)	6.34	6.77	6.94	7.17	96
Δ	**-1.10**	**-0.50**	**-0.50**	**-0.52**	
LH=2-phenylthiazole (**115**)	7.45	7.45	7.45	7.95	
$[RhL_2Cl]_2$	6.02	6.72	6.83	7.45	
Δ	**-1.43**	**-0.73**	**-0.62**	**-0.50**	
RhL_2(acac)	6.30	6.80	6.88	7.49	
Δ	**-1.15**	**-0.65**	**-0.57**	**-0.46**	
RhL_2(dbm) (**116**)	6.41	6.85	6.92	7.52	
Δ	**-1.04**	**-0.60**	**-0.53**	**-0.43**	

	H-3'	*H-4'*	*H-5'*	*H-6'*	*Reference*
LH=2-phenylindazole (**117**)	7.54	7.41	7.54	7.92	
$[RhL_2Cl]_2$	5.75	6.50	6.87	7.38	
Δ	**-1.79**	**-0.91**	**-0.67**	**-0.54**	
RhL_2(acac) (**118**)	6.08	6.65	6.89	7.37	
Δ	**-1.46**	**-0.76**	**-0.65**	**-0.55**	
RhL_2(dbm) (**119**)	6.20	6.72	6.98	7.45	
Δ	**-1.34**	**-0.69**	**-0.56**	**-0.47**	
RhL_2(bac) (**120**)	6.12	6.69	6.95	7.41	
	6.18			7.44	
LH=2-phenylbenzoxazole (**121**)	7.55	7.55	7.55	8.27	
$[RhL_2Cl]_2$ (**122**)	6.22	6.74	7.07	7.28	
Δ	**-1.33**	**-0.81**	**-0.48**	**-0.99**	
RhL_2(acac) (**123**)	6.54	6.86	6.97	7.73	
Δ	**-1.01**	**-0.69**	**-0.58**	**-0.54**	
RhL_2(dbm) (**124**)	6.66	6.92	7.02	7.77	
Δ	**-0.89**	**-0.63**	**-0.53**	**-0.50**	
RhL_2(bac) (**125**)	6.59	6.89	6.99	7.74	
	6.61		7.00	7.76	
LH=2-phenylbenzothiazole (**126**)	7.51	7.51	7.51	8.11	
$[RhL_2Cl]_2$	5.99	6.56	6.85	7.57	
Δ	**-1.52**	**-0.95**	**-0.66**	**-0.54**	
LH=2-phenyl-1,2,3-triazole (**127**)	7.42	7.36	7.42	8.09	
$[RhL_2Cl]_2$	6.13	6.90	7.08	7.69	
Δ	**-1.29**	**-0.46**	**-0.34**	**-0.40**	
RhL_2(acac) (**128**)	6.19	6.83	7.01	7.66	
Δ	**-1.23**	**-0.53**	**-0.41**	**-0.43**	
RhL_2(dbm) (**129**)	6.30	6.89	7.06	7.70	
Δ	**-1.12**	**-0.47**	**-0.36**	**-0.39**	
RhL_2(bac) (**130**)	6.23	6.86	7.03	7.67	
	6.26		7.04		
LH=2-phenylpyridine (**201**)	7.47	7.40	7.47	7.99	
$[RhL_2Cl]_2$	5.95	6.65	6.82	7.55	
Δ	**-1.52**	**-0.75**	**-0.65**	**-0.44**	
RhL_2(acac)	6.29	6.77	6.89	7.59	
Δ	**-1.18**	**-0.63**	**-0.58**	**-0.40**	
RhL_2(dbm)	6.40	6.82	6.94	7.63	
Δ	**-1.07**	**-0.58**	**-0.53**	**-0.36**	
RhL_2(bac)	6.34	6.80	6.92	7.62	
	6.36				
LH=2-phenylquinoline (**203**)	7.52	7.48	7.52	8.17	
RhL_2(acac) (**206**)	6.54	6.70	7.01	7.87	
Δ	**-0.98**	**-0.78**	**-0.51**	**-0.30**	

	H-3'	*H-4'*	*H-5'*	*H-6'*	*Reference*
LH=benzo[*h*]quinoline (**462**)	7.74	7.68	7.89		96
$[RhL_2Cl]_2$	5.99	6.88	7.26		96
Δ	**-1.75**	**-0.80**	**-0.63**		
RhL_2(acac)	6.23	6.98	7.30		96
Δ	**-1.51**	**-0.70**	**-0.59**		
RhL_2(dbm)	6.36	7.05	7.36		96
Δ	**-1.38**	**-0.63**	**-0.53**		
RhL_2(bac)	6.28	7.02	7.33		96
	6.31		7.34		
LH=2,3-diphenylquinoxaline (**458**)	7.35	7.35	7.35	7.53	
$[RhL_2Cl]_2$	5.73	6.26	6.50	6.90	
Δ	**-1.62**	**-1.09**	**-0.85**	**-0.63**	
RhL_2(acac) (**460**)	6.52	6.60	6.67	7.08	
Δ	**-0.83**	**-0.75**	**-0.68**	**-0.45**	
LH=dibenzo[*a*,*c*]phenazine (**459**)	7.75	7.81	8.58		
$[RhL_2Cl]_2$	6.14	6.94	7.92		
Δ	**-1.61**	**-0.87**	**-0.66**		
RhL_2(acac) (**461**)	6.49	7.03	8.01		
Δ	**-1.26**	**-0.78**	**-0.57**		

Table 5.6 ^{13}C NMR chemical shifts of the phenyl ring for the free ligands and cyclorhodated complexes where Δ = CIS = δ(complex(ppm)) - δ(free ligand(ppm)).

	C-3'	*C-4'*	*C-5'*	*C6'*	*Reference*
LH=1-phenylpyrazole (**116**)	129.4	126.4	129.4	119.2	96
RhL_2(acac)	135.0	125.4	122.4	110.9	96
Δ	**5.6**	**-1.0**	**-7.0**	**-8.3**	
RhL_2(dbm)	135.2	125.3	122.4	111.0	96
Δ	**5.8**	**-1.1**	**-7.0**	**-8.2**	
LH=2-phenylthiazole (**115**)	129.1	130.4	129.1	126.7	
RhL_2(acac)	134.1	129.1	122.3	124.0	
Δ	**5.0**	**-1.3**	**-6.8**	**-2.7**	
RhL_2(dbm) (**116**)	134.2	130.1	122.1	123.9	
Δ	**5.1**	**-0.3**	**-7.0**	**-2.8**	
LH=2-phenylindazole (**117**)	129.5	127.8	129.5	120.9	
RhL_2(acac) (**118**)	135.7	126.6	122.8	113.0	
Δ	**6.2**	**-1.2**	**-6.7**	**-7.9**	
RhL_2(dbm) (**119**)	135.9	126.5	122.6	112.8	
Δ	**6.4**	**-1.3**	**-6.9**	**-8.1**	
RhL_2(bac) (**120**)	135.7	126.5	122.6	112.8	
	135.9	126.7	122.8	113.0	

	C-3'	*C-4'*	*C-5'*	*C6'*	*Reference*
LH=2-phenylbenzoxazole (**121**)	128.8	131.4	128.8	127.6	
RhL_2(acac) (**123**)	134.5	130.8	122.6	125.4	
Δ	**5.7**	**-0.6**	**-6.2**	**-2.2**	
RhL_2(dbm) (**124**)	134.6	130.6	122.4	125.3	
Δ	**5.8**	**-0.8**	**-6.4**	**-2.3**	
RhL_2(bac) (**125**)	134.4	130.6	122.4	125.2	
	134.7	130.8	122.6	125.5	
LH=2-phenyl-1,2,3-triazole (**127**)	129.2	127.5	129.2	118.9	
RhL_2(acac) (**128**)	134.1	127.4	123.5	114.3	
Δ	**4.9**	**-0.1**	**-5.7**	**-4.6**	
RhL_2(dbm) (**129**)	134.2	127.3	123.4	114.3	
Δ	**5.0**	**-0.2**	**-5.8**	**-4.6**	
RhL_2(bac) (**130**)	134.0	127.3	123.4	114.3	
	134.2	127.5	123.5	114.4	
LH=2-phenylpyridine (**201**)	128.7	128.9	128.7	126.9	
RhL_2(acac)	133.7	128.9	122.0	123.6	
Δ	**5.0**	**0.0**	**-6.7**	**-3.3**	
RhL_2(dbm)	133.9	128.7	121.8	123.4	
Δ	**5.2**	**-0.2**	**-6.9**	**-3.5**	
RhL_2(bac)	133.7	128.7	121.8	123.4	
	133.9	128.9	122.0	123.6	
LH=2-phenylquinoline (**203**)	128.8	129.3	128.8	127.5	
RhL_2(acac) (**206**)	136.1	128.5	122.2	125.5	
Δ	**7.3**	**-0.8**	**-6.6**	**-2.0**	
LH=benzo[*h*]quinoline (**462**)	127.1	128.2	127.8		96
RhL_2(acac)	131.2	128.4	120.1		96
Δ	**4.1**	**0.2**	**-7.7**		
RhL_2(dbm)	131.1	128.1	119.8		96
Δ	**4.0**	**-0.1**	**-8.0**		
RhL_2(bac)	130.9	129.2	119.6		96
	131.1	129.3	119.8		

Table 5.7 Results of a statistical analysis of the data in table 5.5, the ^{1}H NMR chemical shifts of the phenyl ring of the free ligands and cyclorhodated complexes.

	H-3'	*H-4'*	*H-5'*	*H-6'*
# $[RhL_2Cl]_2$ COMPLEXES (Five-membered rhodacycles)	10	10	10	8
Mean CIS (ppm)	-1.53	-0.80	-0.62	-0.58
Standard deviation	0.16	0.16	0.13	0.17
# RhL_2(acac) COMPLEXES (Five-membered rhodacycles)	10	10	10	8
Mean CIS (ppm)	-1.18	-0.68	-0.57	-0.46
Standard deviation	0.20	0.08	0.07	0.08
# RhL_2(dbm) COMPLEXES (Five-membered rhodacycles)	7	7	7	6
Mean CIS (ppm)	-1.13	-0.59	-0.51	-0.45
Standard deviation	0.16	0.07	0.06	0.06

Table 5.8 Results of a statistical analysis of the data in table 5.6, the ^{13}C NMR chemical shifts of the phenyl ring of the free ligands and cyclorhodated complexes.

	C-3'	*C-4'*	*C-5'*	*C-6'*
# RhL_2(acac) COMPLEXES (Five-membered rhodacycles)	8	8	8	7
Mean CIS (ppm)	+5.5	-0.6	-6.7	-4.4
Standard deviation	0.9	0.5	0.5	2.5
# RhL_2(dbm) COMPLEXES (Five-membered rhodacycles)	7	7	7	6
Mean CIS (ppm)	+5.3	-0.6	-6.9	-4.9
Standard deviation	0.7	0.5	0.6	2.4

Tables 5.5 and 5.6 list the assigned ^{1}H and ^{13}C NMR spectra respectively for the ligand LH and the cyclorhodated complexes—$[RhL_2Cl]_2$; $RhL_2(acac)$; $RhL_2(dbm)$; and $RhL_2(bac)$—along with the CIS; $\Delta = \delta(complex) - \delta(free\ ligand)$. In addition, tables 5.7 and 5.8 list the results of a statistical analysis of the CIS data from tables 5.5 and 5.6 respectively.

As with the statistical analyses of the cyclopalladated complexes (*vide supra*), the analyses of CIS values observed in the spectra of cyclorhodated complexes show consistent patterns, despite the relatively small sample size. Consideration of these trends, both independently and relative to those for the cyclopalladated complexes, is both interesting and informative.

Perhaps the most obvious difference between the rhodium(III) system and the palladium(II) system is the coordination geometry, octahedral and square planar respectively. The octahedral geometry about the rhodium(III) centre means that the two cyclometallated moieties in such complexes experience inter-ligand through space effects that are absent in the analogous palladium complexes. This is most obviously illustrated by the observed mean CIS for H-3' and C-3'. In the cyclopalladated complexes, both of these atoms exhibit a consistent, small downfield shift due to interaction with the acetylacetonate oxygen lone pair. However, for H-3' in cyclorhodated complexes, a consistent and very large upfield shift is observed. This difference is a result of interaction between this proton and the shielding ring current of the coordinated heterocycle of the other cyclometallated ligand, which is coordinated *cis* to the cyclorhodated ring. This observation is consistent with observations made of analogous octahedral rhodium(III) and iridium(III) complexes.[107,109] Since the through-space ring current anisotropy effects are less important in ^{13}C NMR, C-3' shows a consistent downfield shift.

Carbons C-5', *para* to the rhodium atom again shows the consistent and relatively large upfield shift observed for the equivalent position in cyclopalladated complexes. In the cyclorhodated acetylacetonate complexes, however, this shift—and the CIS of the attached proton—is of greater magnitude (-6.7 ppm) than that in the

corresponding cyclopalladated acetylacetonate complexes (-4.2 ppm), suggesting that the metal-to-ligand back-bonding ability of rhodium(III) is greater than that of palladium(II). Although H-4' shows a significant upfield mean CIS (-0.68 ppm for $RhL_2(acac)$) this is not the case with C-4' (-0.6 ppm) and this suggests that the shift of H-4' is also influenced by the shielding ring current of the other cyclorhodated ligand.

Carbons C-6' and their attached protons, H-6', again show relatively inconsistent CIS values, those observed for H-6' being somewhat more consistent than those for C-6'. That these shifts are perhaps more consistent than those observed for the cyclopalladated complexes, is most probably a reflection of the greater structural diversity of the ligands in the latter series, than of any inherent difference between the two systems.

The differences in observed CIS values between $[RhL_2Cl]_2$, $RhL_2(acac)$ and $RhL_2(dbm)$ for atoms in equivalent positions are relatively small. This is to be expected because the cyclorhodated phenyl rings are the least susceptible to the difference in through space effects that result from a change in ligand coordinated to the rhodium at the sites *trans* to them.

5.4 CONCLUSION

It is hoped that these CIS values will prove useful for other workers, since they allow relatively accurate prediction of the NMR chemical shifts of cyclopalladated and cyclorhodated compounds from a knowledge of the assignments of the starting ligands. This is particularly true in the case of predicting the CIS of H-4' and C-5' in cyclopalladated complexes. Such predictions can be useful, for example, to distinguish between structural isomers resulting from the cyclometallation of ligands that can undergo the reaction at more than one site.[110]

Conclusion

CONCLUSION

Over the past three decades there has been increasing interest in the synthesis and study of cyclometallated compounds. Being at the interface between the traditional disciplines of organometallic and coordination chemistry, cyclometallated complexes have a unique combination of properties, and have attracted interest from researchers in many fields, both applied and theoretical. Complexes of this type have found a wide variety of applications and, with the increasing amount of research being reported, these can only be expected to increase.

This thesis has described the preparations of a number of new cyclopalladated and cyclorhodated complexes, all of which have been fully characterised. The ^{1}H and ^{13}C NMR data accumulated in the course of this research has been used to refine, in the case of cyclopalladated acetylacetonate complexes, and to elucidate, in the case of cyclorhodated ß-diketonate complexes, trends in the CIS values observed, such that relatively accurate predictions of chemical shifts for specific positions in the ligand, upon cyclometallation, may be made. In addition, the single crystal X-ray structure determinations of several complexes, both cyclometallated and non-cyclometallated, have been reported and their significance discussed.

Syntheses have been developed for the preparation of two doubly cyclometallated analogues of quaterpyridine. Their cyclopalladated complexes have also been prepared and, as a result, the foundations for further research of these and related ligands have been laid.

A series of phenoxy- and phenylthio-substituted heterocycles have been prepared with a view to the targeted synthesis of six- and seven-membered metallocycles, reports of which are relatively uncommon. Despite the limited success of this strategy, the target ligands have been shown to possess interesting coordination chemistry. In particular, trends in temperature dependent behaviour have been established and a possible explanation for these observations proposed.

Experimental

INSTRUMENTATION AND REAGENTS

Infrared spectra were recorded on a Perkin Elmer 1600 FTIR or Shimadzu 8201 FTIR spectrophotometer. Mass spectra were obtained with a Kratos MS80RFA spectrometer with a Mac 3 data system. Electron impact (EI) spectra were obtained at 70 eV with a source temperature of 150°C. Fast atom bombardment (FAB) spectra were acquired in a nitrobenzyl alcohol matrix using an Iontech ZN1FW FAB gun operated at 8 KV and 2 mA. Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were performed by the Chemistry Department, University of Otago, Dunedin. For a number of the metallated complexes low carbon analyses are consistently observed and this is attributed to the non-stoichiometric formation of metal carbides during the combustion process, as noted in the literature.[204]

^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer with a 3 mm or 5 mm probe and are referenced to the Me_4Si signal for $CDCl_3$ solutions and to the residual protonated solvent signal for CD_3CN and d_6-DMSO solutions. ^{13}C NMR spectra were recorded on a Varian Unity 300 or a Varian XL-300 spectrometer with a 3 mm or 5mm probe and are referenced to the solvent signal. All other one-dimensional and two-dimensional NMR experiments were performed on a Varian Unity 300 spectrometer using standard pulse sequences and parameters.

Radial chromatography was performed on a Chromatotron (Harrison and Harrison) using Merck type 60 P.F.254 silica gel. Column chromatography was performed with silica gel (grade 923, 100-200 mesh). Unless otherwise stated petroleum ether refers to that fraction boiling at 50-70°C and ether to diethyl ether. Solvents were purified according to standard literature procedures.

Thallium acetylacetonate and dibenzoylmethanate were prepared from thallium carbonate and acacH or dbmH according to a literature procedure.[283] Unless otherwise stated, reagents were obtained from commercial sources and were used as received.

GENERAL PROCEDURES

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE:

A solution of one equivalent of palladium chloride and three equivalents of lithium chloride in methanol was refluxed for two hours and then filtered. The filtrate was added to a methanol solution of the ligand and the resultant solution stirred for one to four days. The resultant precipitate was filtered off and washed with methanol then with ether.

(ii) REACTION WITH PALLADIUM ACETATE:

Method A: A solution containing the ligand and one or two equivalents of palladium acetate in glacial acetic acid was refluxed for one hour. The acetic acid was then removed under reduced pressure. The resultant μ-diacetato dipalladium complex was then converted to the μ-dichloro dipalladium complex by stirring with an acetone/water (60/40, v/v) solution containing excess lithium chloride (four equivalents) for up to four days. The resultant precipitate was filtered off and washed with acetone then with ether.

Method B: A solution containing the ligand and one or two equivalents of palladium acetate in benzene was degassed by passing a stream of nitrogen bubbles through it for five minutes and then heated at 60°C under an atmosphere of nitrogen for 24 hours. The benzene was then removed under reduced pressure and the residue taken up in chloroform and filtered. The filtrate was stripped of solvent under reduced pressure and the residue stirred with an acetone/water (60/40, v/v) solution containing excess lithium chloride (four equivalents) for up to four days. The resultant precipitate of μ-dichloro dipalladium complex was filtered off and washed with acetone then with ether.

(iii) REACTION WITH RHODIUM TRICHLORIDE:

A solution containing rhodium trichloride trihydrate and two equivalents of the ligand in 2-methoxyethanol was stirred under reflux for two days to give a suspension

which was allowed to cool to room temperature and then refrigerated. The resultant precipitate was then filtered off.

(iv) PREPARATION OF ß-DIKETONATE COMPLEXES:

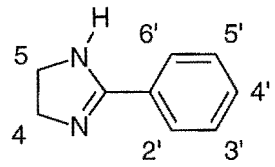
Method A: Excess ß-diketone was added to a freshly prepared solution of sodium methoxide in methanol and the resultant solution of sodium ß-diketonate added to a suspension of the chloro-bridged dimer in methanol and the mixture stirred for one to four days. The precipitated ß-diketonate complex was filtered and washed with methanol then with ether.

Method B: The chloro-bridged dimer was added to a solution of two equivalents of thallium ß-diketonate in dichloromethane and the resultant solution stirred for 24 hours. The precipitate of thallium chloride was filtered off using a plug of anhydrous magnesium sulfate and the dichloromethane removed from the filtrate under reduced pressure. The residue was taken up in chloroform and vapour diffusion of petroleum ether into this solution gave the ß-diketonate complex, which was filtered off and washed with pentane.

PREPARATION AND SPECTRA OF LIGANDS AND COMPLEXES

2-Phenylimidazoline, 101.

101 was obtained commercially (Aldrich). ^{1}H NMR ($CDCl_3$): δ 3.72 (s, 4H, H-4 and H-5), 4.93 (br s, 1H, N-H), 7.35 (t, 2H, H-3' and H-5'), 7.41 (t, 1H, H-4'), 7.77 (d, 2H, H-2' and H-6'). ^{13}C NMR ($CDCl_3$): δ 50.05 (C-4 and C-5), 125.21 (C-1'), 126.83 (C-2' and C-6'), 128.20 (C-3' and C-5'), 130.38 (C-4'), 164.73 (C-2).



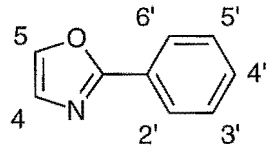
101

(i) REACTION WITH PALLADIUM ACETATE

101 and palladium acetate were reacted according to method B to give **104**[53] which was reacted with thallium acetylacetonate, as in the general procedure, to give Pd(**101**-H)(acac), **105**, in 8% overall yield. Mp 195-199°C. Anal. Calcd for $C_{14}H_{16}N_2O_2Pd$: C, 47.95; H, 4.60; N, 7.99; Found: C, 47.80; H, 4.48; N, 8.04%. ^1H NMR ($CDCl_3$): δ 1.99 (s, 3H, acac-CH_3), 2.06 (s, 3H, acac-CH_3), 3.76 (m, 2H, H-5), 3.91 (m, 2H, H-4), 5.24 (br s, 1H, N-H), 5.36 (s, 1H, acac-CH), 7.01 (m, 2H, H-5' and H-6'), 7.18 (m, 1H, H-4'), 7.57 (d, 1H, H-3'). ^{13}C NMR ($CDCl_3$): δ 27.57 and 27.85 (acac-CH_3), 44.47 (C-5), 50.60 (C-4), 100.26 (acac-CH), 123.25 (C-5'), 123.58 (C-6'), 129.79 (C-4'), 130.95 (C-3'), 134.92 (C-1'), 152.11 (C-2'), 173.92 (C-2), 186.13 and 187.86 (acac-CO).

2-Phenyloxazole, 109.

109 was prepared by the condensation of vinylene carbonate and benzamide in polyphosphoric acid as previously reported.[68] ^1H NMR ($CDCl_3$): δ 7.24 (br s, 1H, H-4), 7.46 (m, 3H, H-3', H-4' and H-5'), 7.72 (br s, 1H, H-5), 8.06 (m, 2H, H-2' and H-6'). ^{13}C NMR ($CDCl_3$): δ 126.35 (C-2' and C-6'), 127.54 (C-1'), 128.41 (C-4), 128.78 (C-3' and C-5'), 130.35 (C-4'), 138.57 (C-5), 161.99 (C-2).



109

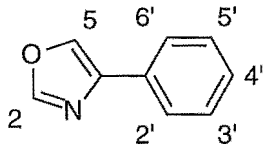
(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

109 and one equivalent of lithium tetrachloropalladate were reacted according to the general procedure to give Pd(**109**)$_2Cl_2$, **112**, in 36% yield. Mp >300°C. Anal. Calcd for $C_{18}H_{14}N_2O_2Cl_2Pd$: C, 46.23; H, 3.02; N, 5.99; Cl, 15.16; Found: C, 46.28; H, 2.72; N, 5.92; Cl, 15.19%. IR (KBr pellet): ν_{max} 1567, 1487, 1262, 916, 785, 712 and 683 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.60 (t, 2H, H-3' and H-5'), 7.65 (t, 1H, H-4'), 7.70 (d, 1H, H-4), 7.83 (d, 1H, H-5), 8.94 (d, 2H, H-2' and H-6'). ^{13}C NMR ($CDCl_3$): δ

124.46 (C-1'), 128.89 (C-2' and C-6'), 129.00 (C-3' and C-5'), 129.48 (C-4), 132.42 (C-4'), 139.53 (C-5), 162.86 (C-2).

4-Phenyloxazole, 110.

110 was prepared by the reaction of 2-bromoacetophenone with ammonium formate in formic acid as previously reported.[73] ^{1}H NMR ($CDCl_3$): δ 7.32 (t, 1H, H-4'), 7.42 (t, 2H, H-3' and H-5'), 7.75 (d, 2H, H-2' and H-6'), 7.95 (d, 1H, H-2), 7.95 (d, 1H, H-5). ^{1}H NMR (d_6-DMSO): δ 7.42 (t, 1H, H-4'), 7.53 (t, 2H, H-3' and H-5'), 7.91 (d, 2H, H-2' and H-6'), 8.57 (s, 1H, H-2), 8.72 (s, 1H, H-5). ^{13}C NMR ($CDCl_3$): δ 125.53 (C-2' and C-6'), 128.17 (C-4'), 128.74 (C-3' and C-5'), 130.65 (C-1'), 133.69 (C-5), 140.31 (C-4), 151.34 (C-2). ^{13}C NMR (d_6-DMSO): δ 125.34 (C-2' and C-6'), 128.08 (C-4'), 128.90 (C-3' and C-5'), 130.84 (C-1'), 135.17 (C-5), 139.35 (C-4), 152.72 (C-2).



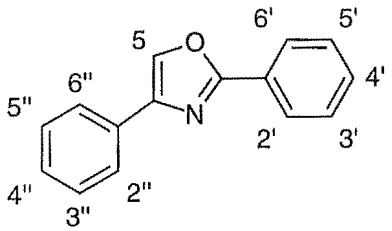
110

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

110 was reacted with one equivalent of lithium tetrachloropalladate according to the general procedure to give Pd(**110**)$_2$Cl$_2$, **113**, in 77% yield. Mp 262-265°C (dec.). Anal. Calcd for $C_{18}H_{14}N_2O_2Cl_2Pd$: C, 46.23; H, 3.02; N, 5.99; Cl, 15.16; Found: C, 45.93; H, 3.02; N, 5.94; Cl, 15.40%. IR (KBr pellet): ν_{max} 1527, 1488, 1169, 1073, 908, 841, 762, 690, 678, 613 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.53 (m, 3H, H-3', H-4' and H-5'), 7.81 (s, 1H, H-5), 8.18 (m, 2H, H-2' and H-6'), 8.50 (s, 1H, H-2). ^{1}H NMR (d_6-DMSO): δ 7.43 (t, 1H, H-4'), 7.54 (t, 2H, H-3' and H-5'), 7.90 (d, 2H, H-2' and H-6'), 8.57 (s, 1H, H-2), 8.73 (s, 1H, H-5). ^{13}C NMR (d_6-DMSO): δ 125.28 (C-2' and C-6'), 128.07 (C-4'), 128.90 (C-3' and C-5'), 130.78 (C-1'), 135.20 (C-5), 139.26 (C-4), 152.74 (C-2).

2,4-Diphenyloxazole, 111.

111 was prepared by the reaction of 2-bromoacetophenone and benzamide as previously reported.[75] Purification of the crude solid was by recrystallisation from ethanol, rather than by distillation, and the oxazole was obtained as white needles. Yield 13.3%. Mp 103.5-105°C (lit.[75] 102.5-103.5°C). Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33; Found: C, 81.19; H, 5.05; N, 6.40%. IR (KBr pellet): ν_{max} 1554, 1489, 1448, 1124, 1070, 943, 931, 783, 757, 719, 706 and 693 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33 (t, 1H, H-4"), 7.43 (t, 2H, H-3" and H-5"), 7.47 (m, 3H, H-3', H-4' and H-5'), 7.83 (d, 2H, H-2" and H-6"), 7.95 (s, H-5), 8.13 (m, 2H, H-2' and H-6'). ^1H NMR (d_6-DMSO): δ 7.45 (t, 1H, H-4"), 7.56 (t, 2H, H-3" and H-5"), 7.67 (m, 3H, H-3', H-4' and H-5'), 7.97 (d, 2H, H-2" and H-6"), 8.16 (m, 2H, H-2' and H-6'), 8.80 (s, H-5). ^{13}C NMR ($CDCl_3$): δ 125.62 (C-2" and C-6"), 126.49 (C-2' and C-6'), 127.48 (C-1"), 128.09 (C-4"), 128.73 (C-3', C-5', C-3" and C-5"), 130.37 (C-4'), 131.11 (C-1'), 133.42 (C-5), 141.99 (C-2), 161.91 (C-4). ^{13}C NMR (d_6-DMSO): δ 125.44 (C-2" and C-6"), 126.25 (C-2' and C-6'), 126.91 (C-1"), 128.34 (C-4"), 129.02 (C-3" and C-5"), 129.38 (C-3' and C-5'), 130.86 (C-1'), 130.97 (C-4'), 135.69 (C-5), 141.21 (C-2), 161.19 (C-4).



111

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

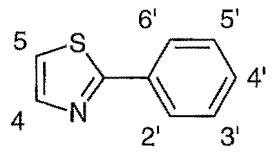
Lithium tetrachloropalladate was reacted with two equivalents of **111** according to the general procedure to give Pd(**111**)$_2$Cl$_2$ in 42% yield. Mp=220-221°C. Calcd for $C_{30}H_{22}N_2O_2{}^{35}Cl{}^{108}Pd$: M^+, 585.0409; Found (FAB):M^+, 585.0421. IR (KBr pellet): ν_{max} 1592, 1539, 1480, 1448, 1360, 934, 778, 758, 721, 694 cm^{-1}.

(ii) REACTION WITH MERCURIC ACETATE

A solution of **111** (204 mg, 0.92 mmol) and mercuric acetate (262 mg, 0.82 mmol) in ethanol (15 cm^3) and acetic acid (0.2 cm^3) was stirred under reflux for 5 days. The solution was cooled and the resultant precipitate filtered off, washed with chilled ethanol (10 cm^3) and then dried under reduced pressure to give Hg(**111**-H)(OAc), **114**, in 67% yield. Mp 181.5-184.5°C. Anal. Calcd for $C_{17}H_{13}NO_3Hg$: C, 42.55; H, 2.73; N, 2.92; Found: C, 42.03; H, 2.39; N, 3.04%. IR (KBr pellet): ν_{max} 1649, 1610, 1554, 1488, 1446, 1368, 1279, 970, 780, 716, 692 cm^{-1}. ^1H NMR (d_6-DMSO): δ 2.07 (s, 3H, *CH*$_3$COO), 7.44 (t, 1H, H-4"), 7.53 (t, 2H, H-3" and H-5"), 7.67 (m, 3H, H-3', H-4' and H-5'), 8.15 (d, 4H, H-2', H-6', H-2" and H-6"). ^{13}C NMR (d_6-DMSO): δ 23.01 (*C*H$_3$COO), 125.88 (C--2" and C-6"), 126.11 (C-2' and C-6'), 127.32 (C-1"), 128.18 (C-4"), 128.80 (C-3" and C-5"), 129.38 (C-3' and C-5'), 130.71 (C-4'), 132.14 (C-1'), 148.60 (C-2), 164.02 (C-4), 175.09 (CH$_3$*C*OO).

2-Phenylthiazole, 115.

115 was available in the department. ^1H NMR ($CDCl_3$): δ 7.36 (d, 1H, H-5), 7.45 (m, 3H, H-3', H-4' and H-5'), 7.93 (d, 1H, H-4), 7.95 (m, 2H, H-2' and H-6'). ^{13}C NMR ($CDCl_3$): δ 119.04 (C-5), 126.73 (C-2' and C-6'), 129.05 (C-3' and C-5'), 130.42 (C-4'), 142.79 (C-4).



115

(i) REACTION WITH RHODIUM TRICHLORIDE

Reaction of **115** with rhodium trichloride trihydrate gave [Rh(**115**-H)$_2$Cl]$_2$ in 56% yield. A sample was recrystallised from chloroform/petroleum ether for elemental analysis. Mp >300°C. Anal. Calcd for $C_{36}H_{24}N_4S_4Cl_2Rh_2.CHCl_3$: C, 42.86; H, 2.43; N, 5.40; Cl, 17.09; Found: C, 42.43; H, 2.45; N, 5.57; Cl, 17.56%. ^1H NMR ($CDCl_3$):

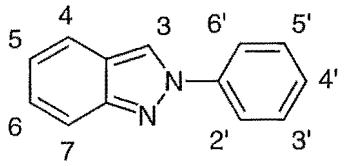
δ 6.02 (d, 1H, H-3'), 6.72 (t, 1H, H-4'), 6.83 (t, 1H, H-5'), 7.17 (d, 1H, H-5), 7.45 (d, 1H, H-6'), 8.08 (d, 1H, H-4).

Ligand exchange of [Rh(**115**-H)$_2$Cl]$_2$ with thallium acetylacetonate gave Rh(**115**-H)$_2$(acac) in 29% yield. Mp >300°C. Anal. Calcd for $C_{23}H_{19}N_2O_2S_2Rh.{}^1/_2H_2O$: C, 51.98; H, 3.79; N, 5.27; Found: C, 51.99; H, 3.67; N, 5.28%. ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 6H, acac-CH_3), 5.21 (s, 1H, acac-CH), 6.30 (d, 2H, H-3'), 6.80 (t, 2H, H-4'), 6.88 (t, 2H, H-5'), 7.35 (d, 2H, H-5), 7.49 (d, 2H, H-6'), 7.70 (d, 2H, H-4). ^{13}C NMR ($CDCl_3$): δ 28.79 (acac-CH_3), 98.11 (acac-CH), 116.29 (C-5), 122.28 (C-5'), 124.00 (C-6'), 129.11 (C-4'), 134.10 (C-3'), 140.02 (C-4), 187.67 (acac-CO).

Ligand exchange of [Rh(**115**-H)$_2$Cl]$_2$ with thallium dibenzoylmethanate gave Rh(**115**-H)$_2$(dbm), **116**, in 46% yield. Mp 231°C (dec.). Anal. Calcd for $C_{33}H_{23}N_2O_2S_2Rh$: C, 61.03; H, 3.59; N, 4.33; Found: C, 58.67; H, 3.57; N, 4.17%. ^{1}H NMR ($CDCl_3$): δ 6.41 (d, 2H, H-3'), 6.54 (s, 1H, dbm-CH), 6.85 (t, 2H, H-4'), 6.92 (t, 2H, H-5'), 7.25 (d, 2H, H-5), 7.31 (t, 4H, dbm-*meta*), 7.37 (t, 2H, dbm-*para*), 7.52 (d, 2H, H-6'), 7.73 (d, 2H, H-4), 7.82 (d, 4H, dbm-*ortho*). ^{13}C NMR ($CDCl_3$): δ 92.63 (dbm-CH), 116.22 (C-5), 122.07 (C-5'), 123.85 (C-6'), 127.10 (dbm-*ortho*), 128.03 (dbm-*meta*), 130.05 (C-4' and dbm-*para*), 134.20 (C-3'), 140.09 (C-4), 182.79 (dbm-CO).

2-Phenylindazole, 117.

117 was available in the department. ^{1}H NMR ($CDCl_3$): δ 7.12 (t, 1H, H-5), 7.33 (t, 1H, H-6), 7.41 (t, 1H, H-4'), 7.54 (t, 2H, H-3' and H-5'), 7.72 (d, 1H, H-4), 7.80 (d, 1H, H-7), 7.92 (d, 2H, H-2' and H-6'), 8.43 (s, 1H, H-3). ^{13}C NMR ($CDCl_3$): δ 117.85 (C-7), 120.33 (C-3 and C-4), 120.85 (C-2' and C-6'), 122.36 (C-5), 126.74 (C-6), 127.78 (C-4'), 129.45 (C-3' and C-5').



117

(i) REACTION WITH RHODIUM TRICHLORIDE

Reaction of **117** with rhodium trichloride trihydrate gave [Rh(**117**-H)$_2$Cl]$_2$ in 65% yield. ^{1}H NMR ($CDCl_3$): δ 5.75 (d, 1H, H-3'), 6.50 (t, 1H, H-4'), 6.55 (t, 1H, H-6), 6.80 (t, 1H, H-5), 6.87 (t, 1H, H-5'), 7.38 (d, 1H, H-6'), 7.41 (d, 1H, H-4), 8.34 (d, 1H, H-7), 8.55 (s, 1H, H-3).

Ligand exchange of [Rh(**117**-H)$_2$Cl]$_2$ with sodium acetylacetonate gave Rh(**117**-H)$_2$(acac), **118**, in 57% yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp 323°C (dec.). Anal. Calcd for $C_{31}H_{25}N_4O_2Rh$: C, 63.27; H, 4.28; N, 9.52; Found: C, 62.84; H, 4.01; N, 9.36%. ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 6H, acac-CH_3), 5.28 (s, 1H, acac-CH), 6.08 (d, 2H, H-3'), 6.65 (t, 2H, H-4'), 6.89 (t, 2H, H-5'), 7.21 (t, 2H, H-5), 7.37 (d, 2H, H-6'), 7.37 (t, 2H, H-6), 7.74 (d, 4H, H-4 and H-7), 8.62 (s, 2H, H-3). ^{13}C NMR ($CDCl_3$): δ 28.78 (acac-CH_3), 99.10 (acac-CH), 112.96 (C-6'), 115.59 (C-7), 118.65 (C-3), 120.77 (C-4), 122.79 (C-5'), 122.95 (C-5), 126.63 (C-4'), 128.49 (C-6), 135.68 (C-3'), 187.93 (acac-CO).

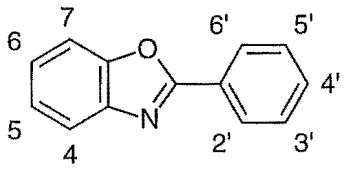
Ligand exchange of [Rh(**117**-H)$_2$Cl]$_2$ with sodium dibenzoylmethanate gave Rh(**117**-H)$_2$(dbm), **119**, in 88% yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp >300°C. Anal. Calcd for $C_{41}H_{29}N_4O_2Rh.{}^1/_2H_2O$: C, 68.24; H, 4.19; N, 7.76; Found: C, 68.11; H, 3.88; N, 7.84%. ^{1}H NMR ($CDCl_3$): δ 6.20 (d, 2H, H-3'), 6.60 (s, 1H, dbm-CH), 6.72 (t, 2H, H-4'), 6.98 (t, 2H, H-5'), 7.12 (t, 2H, H-5), 7.17 (t, 2H, H-6), 7.28 (t, 4H, dbm-*meta*), 7.35 (t, 2H, dbm-*para*), 7.45 (d, 2H, H-6'), 7.71 (d, 2H, H-4), 7.74 (d, 2H, H-7), 7.81 (d, 4H, dbm-*ortho*), 8.64 (s, 2H, H-3). ^{13}C NMR ($CDCl_3$): δ 93.48 (dbm-CH), 112.83 (C-6'), 115.77 (C-7), 118.52 (C-3), 120.61 (C-4), 122.64 (C-5'), 122.94 (C-5), 126.50

(C-4'), 127.20 (dbm-*ortho*), 127.97 (dbm-*meta*), 128.53 (C-6), 129.92 (dbm-*para*), 135.85 (C-3'), 182.95 (dbm-CO).

Ligand exchange of [Rh(**117**-H)$_2$Cl]$_2$ with sodium benzoylacetonate gave Rh(**117**-H)$_2$(bac), **120**, in 65% yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp 311°C (dec.). Anal. Calcd for $C_{36}H_{27}N_4O_2Rh.{}^1/_2H_2O$: C, 65.55; H, 4.28; N, 8.49; Found: C, 65.50; H, 4.02; N, 8.47%. ^{1}H NMR ($CDCl_3$): δ 2.05 (bac-CH_3), 5.93 (bac-CH), 6.12 (d, 1H, H-3'a or H-3'b), 6.18 (d, 1H, H-3'a or H-3'b), 6.69 (t, 2H, H-4'a and H-4'b), 6.95 (t, 2H, H-5'a and H-5'b), 7.17 (m, 2H, H-5a and H-5b), 7.19 (t, 1H, H-6a or H-6b), 7.24 (t, 2H, bac-*meta*), 7.29 (t, 1H, bac-*para*), 7.36 (t, 1H, H-6a or H-6b), 7.41 (d, 1H, H-6'a or H-6'b), 7.44 (d, 1H, H-6'a or H-6'b), 7.69 (d, 1H, H-7a or H-7b), 7.72 (d, 3H, bac-*ortho* and H-4a or H-4b), 7.75 (d, 1H, H-4a or H-4b), 7.79 (d, 1H, H-7a or H-7b), 8.62 (s, 1H, H-3a or H-3b), 8.66 (s, 1H, H-3a or H-3b). ^{13}C NMR ($CDCl_3$): δ 29.53 (bac-CH_3), 96.12 (bac-CH), 112.80 (C-6'a or C-6'b), 112.99 (C-6'a or C-6'b), 115.59 (C-7a or C-7b), 115.77 (C-7a or C-7b), 118.54 (C-3a or C-3b), 118.60 (C-3a or C-3b), 120.64 (C-4a or C-4b), 120.73 (C-4a or C-4b), 122.63 (C-5'a or C-5'b), 122.82 (C-5'a or C-5'b), 122.95 (C-5a and C-5b), 126.48 (C-4'a or C-4'b), 126.67 (C-4'a or C-4'b), 127.12 (bac-*ortho*), 127.89 (bac-*meta*), 128.46 (C-6a or C-6b), 128.56 (C-6a or C-6b), 129.79 (bac-*para*), 135.66 (C-3'a or C-3'b), 135.89 (C-3'a or C-3'b), 181.12 and 189.78 (bac-CO).

2-Phenylbenzoxazole, 121.

121 was available in the department. ^{1}H NMR ($CDCl_3$): δ 7.37 (m, 2H, H-5 and H-6), 7.55 (m, 3H, H-3', H-4' and H-5'), 7.60 (m, 1H, H-7), 7.79 (m, 1H, H-4), 8.27 (m, 2H, H-2' and H-6'). ^{13}C NMR ($CDCl_3$): δ 110.51 (C-7), 119.94 (C-4), 124.49 (C-6), 125.02 (C-5), 127.55 (C-2' and C-6'), 128.82 (C-3' and C-5'), 131.42 (C-4').



121

(i) REACTION WITH RHODIUM TRICHLORIDE

Reaction of **121** with rhodium trichloride trihydrate gave [Rh(**121**-H)$_2$Cl]$_2$, **122**, in 72% yield. ^{1}H NMR ($CDCl_3$): δ 6.22 (d, 1H, H-3'), 6.74 (t, 1H, H-4'), 6.85 (t, 1H, H-5), 6.92 (t, 1H, H-6), 7.07 (t, 1H, H-5'), 7.28 (d, 1H, H-6'), 7.68 (d, 1H, H-7), 8.24 (d, 1H, H-4).

Ligand exchange of **122** with sodium acetylacetonate gave Rh(**121**-H)$_2$(acac) , **123**, in 79% yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp >300°C. Anal. Calcd for $C_{31}H_{25}N_2O_4Rh.{}^1/_2H_2O$: C, 62.11; H, 4.04; N, 4.67; Found: C, 62.03; H, 4.02; N, 4.39%. ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 6H, acac-CH_3), 5.25 (s, 1H, acac-CH), 6.54 (d, 2H, H-3'), 6.86 (t, 2H, H-4'), 6.97 (t, 2H, H-5'), 7.41 (t, 2H, H-5), 7.44 (t, 2H, H-6), 7.59 (d, 2H, H-4), 7.69 (d, 2H, H-7), 7.73 (d, 2H, H-6'). ^{13}C NMR ($CDCl_3$): δ 28.78 (acac-CH_3), 98.83 (acac-CH), 111.33 (C-7), 117.35 (C-4), 122.56 (C-5'), 125.10 (C-5), 125.42 (C-6'), 125.91 (C-6), 130.80 (C-4'), 134.45 (C-3'), 187.89 (acac-CO).

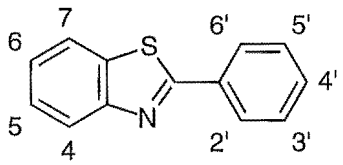
Ligand exchange of **122** with sodium dibenzoylmethanate gave Rh(**121**-H)$_2$(dbm), **124**, in 86% yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp 233°C. Anal. Calcd for $C_{41}H_{27}N_2O_4Rh$: C, 68.92; H, 3.81; N, 3.92; Found: C, 68.87; H, 3.72; N, 4.07%. ^{1}H NMR ($CDCl_3$): δ 6.62 (s, 1H, dbm-CH), 6.66 (d, 2H, H-3'), 6.92 (t, 2H, H-4'), 7.02 (t, 2H, H-5'), 7.20 (t, 2H, H-5), 7.32 (t, 4H, dbm-*meta*), 7.33 (t, 2H, H-6), 7.38 (t, 2H, dbm-*para*), 7.54 (d, 2H, H-4), 7.63 (d, 2H, H-7), 7.77 (d, 2H, H-6'), 7.87 (d, 4H, dbm-*ortho*). ^{13}C NMR ($CDCl_3$): δ 92.77 (dbm-CH), 111.21 (C-7), 117.49 (C-4), 122.38 (C-5'), 124.98 (C-6), 125.26 (C-6'), 125.93 (C-5), 127.22 (dbm-*ortho*), 128.08 (dbm-*meta*), 130.09 (dbm-*para*), 130.63 (C-4'), 134.58 (C-3'), 182.73 (dbm-CO).

Ligand exchange of **122** with sodium benzoylacetonate gave Rh(**121**-H)$_2$(bac) , **125**, in 64% yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp 290-291°C (dec.). Anal. Calcd for $C_{36}H_{25}N_2O_4Rh.{}^1/_2H_2O$: C, 65.36; H, 3.96; N, 4.23; Found: C, 65.57; H, 3.99; N,

3.98%. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 3H, bac-CH_3), 5.94 (s, 1H, bac-CH), 6.59 (d, 1H, H-3'a or H-3'b), 6.61 (d, 1H, H-3'a or H-3'b), 6.89 (t, 2H, H-4'a and H-4'b), 6.99 (t, 1H, H-5'a or H-5'b), 7.00 (t, 1H, H-5'a or H-5'b), 7.21 (d, 1H, H-6a or H-6b), 7.28 (t, 2H, bac-*meta*), 7.32 (t, 1H, bac-*para*), 7.36 (t, 1H, H-5a or H-5b), 7.40 (m, 2H, H-5a or H-5b and H-6a or H-6b), 7.49 (d, 1H, H-4a or H-4b), 7.64 (d, 1H, H-4a or H-4b), 7.65 (d, 1H, H-7a or H-7b), 7.66 (d, 1H, H-7a or H-7b), 7.74 (d, 1H, H-6'a or H-6'b), 7.76 (d, 1H, H-6'a or H-6'b), 7.77 (d, 2H, bac-*ortho*). ^{13}C NMR ($CDCl_3$): δ 29.57 (bac-CH_3), 95.60 (bac-CH), 111.24 (C-7a or C-7b), 111.33 (C-7a or C-7b), 117.33 (C-4a or C-4b), 117.53 (C-4a or C-4b), 122.39 (C-5'a or C-5'b), 122.56 (C-5'a or C-5'b), 125.01 (C-5a or C-5b), 125.07 (C-5a or C-5b), 125.23 (C-6'a or C-6'b), 125.46 (C-6'a or C-6'b), 125.89 (C-6a or C-6b), 125.98 (C-6a or C-6b), 127.17 (bac-*ortho*), 128.00 (bac-*meta*), 129.97 (bac-*para*), 130.60 (C-4'a or C-4'b), 130.81 (C-4'a or C-4'b), 134.39 (C-3'a or C-3'b), 134.65 (C-3'a or C-3'b), 180.84 and 189.77 (bac-CO).

2-Phenylbenzothiazole, 126

126 was available in the department. ^{1}H NMR ($CDCl_3$): δ 7.40 (t, 1H, H-6), 7.51 (m, 4H, H-5, H-3', H-4' and H-5'), 7.92 (d, 1H, H-7), 8.09 (d, 1H, H-4), 8.11 (m, 2H, H-2' and H-6'). ^{13}C NMR ($CDCl_3$): δ 121.56 (C-7), 123.18 (C-4), 125.13 (C-6), 126.25 (C-5), 127.49 (C-2' and C-6'), 128.96 (C-3' and C-5'), 130.89 (C-4').



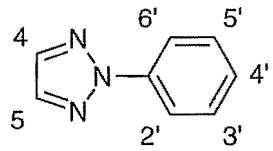
126

(i) REACTION WITH RHODIUM TRICHLORIDE

Reaction of **126** with rhodium trichloride trihydrate gave [Rh(**126**-H)$_2$Cl]$_2$ in 25% yield. ^{1}H NMR ($CDCl_3$): δ 5.99 (d, 1H, H-3'), 6.56 (t, 1H, H-4'), 6.85 (t, 1H, H-5'), 7.02 (m, 2H, H-5 and H-6), 7.41 (d, 1H, H-7), 7.57 (d, 1H, H-6'), 8.94 (d, 1H, H-4).

2-Phenyl-1,2,3-triazole, 127

127 was available in the department. ^{1}H NMR ($CDCl_3$): δ 7.36 (t, 1H, H-4'), 7.42 (t, 2H, H-3' and H-5'), 7.82 (s, 2H, H-4 and H-5), 8.09 (d, 2H, H-2' and H-6'). ^{13}C NMR ($CDCl_3$): δ 118.88 (C-2' and C-6'), 127.48 (C-4'), 129.21 (C-3' and C-5'), 135.41 (C-4 and C-5).



127

(i) REACTION WITH RHODIUM TRICHLORIDE

Reaction of **127** with rhodium trichloride trihydrate gave [Rh(**127**-H)$_2$Cl]$_2$ in 79% yield. ^{1}H NMR ($CDCl_3$): δ 6.13 (br s, 1H, H-3'), 6.90 (t, 1H, H-4'), 7.08 (t, 1H, H-5'), 7.69 (d, 1H, H-6'), 8.25 (s, 1H, H-4), 8.53 (s, 1H, H-5).

Ligand exchange of [Rh(**127**-H)$_2$Cl]$_2$ with sodium acetylacetonate gave Rh(**127**-H)$_2$(acac), **128**, in 76% yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp 240°C (dec.). Anal. Calcd for $C_{21}H_{19}N_6O_2Rh$: C, 51.44; H, 3.91; N, 17.14; Found: C, 49.82; H, 3.86; N, 17.01%. ^{1}H NMR ($CDCl_3$): δ 1.91 (s, 6H, acac-CH_3), 5.25 (s, 1H, acac-CH), 6.19 (d, 2H, H-3'), 6.83 (t, 2H, H-4'), 7.01 (t, 2H, H-5'), 7.66 (d, 2H, H-6'), 7.90 (s, 2H, H-5), 7.97 (s, 2H, H-4). ^{13}C NMR ($CDCl_3$): δ 28.67 (acac-CH_3), 98.17 (acac-CH), 114.32 (C-6'), 123.47 (C-5'), 127.44 (C-4'), 133.36 (C-5), 134.09 (C-4'), 134.86 (C-4), 188.14 (acac-CO).

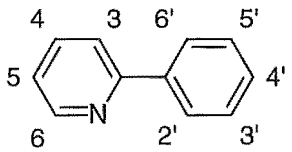
Ligand exchange of [Rh(**127**-H)$_2$Cl]$_2$ with sodium dibenzoylmethanate gave Rh(**127**-H)$_2$(dbm), **129**, in 84% yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp 231-232°C (dec.). Anal. Calcd for $C_{31}H_{23}N_6O_2Rh$: C, 60.60; H, 3.77; N, 13.68; Found: C, 60.46; H, 3.99; N, 13.74%. ^{1}H NMR ($CDCl_3$): δ 6.30 (d, 2H, H-3'), 6.58 (s, 1H, dbm-CH), 6.89 (t, 2H, H-4'), 7.06 (t, 2H, H-5'), 7.33 (t, 4H, dbm-*meta*), 7.40 (t, 2H, dbm-*para*), 7.70 (d, 2H, H-6'), 7.80 (d, 4H, dbm-*ortho*), 7.92 (s, 4H, H-4 and H-5). ^{13}C NMR ($CDCl_3$): δ 92.72 (dbm-CH),

114.28 (C-6'), 123.40 (C-5'), 127.12 (dbm-*ortho*), 127.29 (C-4'), 128.16 (dbm-*meta*), 130.49 (dbm-*para*), 133.41 (C-5), 134.15 (C-3'), 134.90 (C-4), 183.35 (dbm-CO).

Ligand exchange of $[Rh(\mathbf{127}\text{-}H)_2Cl]_2$ with sodium benzoylacetonate gave $Rh(\mathbf{127}\text{-}H)_2(bac)$, **130**, in 63% yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp 223-225°C (dec.). Anal. Calcd for $C_{26}H_{21}N_6O_2Rh$: C, 56.53; H, 3.83; N, 15.21; Found: C, 56.41; H, 4.01; N, 15.15%. ^1H NMR ($CDCl_3$): δ 2.05 (s, 3H, bac-CH_3), 5.91 (s, 1H, bac-CH), 6.23 (d, 1H, H-3'a or H-3'b), 6.26 (d, 1H, H-3'a or H-3'b), 6.86 (t, 2H, H-4'a and H-4'b), 7.03 (t, 1H, H-5'a or H-5'b), 7.04 (t, 1H, H-5'a or H-5'b), 7.29 (t, 2H, bac-*meta*), 7.36 (t, 1H, bac-*para*), 7.67 (d, 2H, H-6'a and H-6'b), 7.70 (d, 2H, bac-*ortho*), 7.86 (s, 1H, H-5a or H-5b), 7.94 (s, 1H, H-4a or H-4b), 7.95 (s, 2H, H-4a or H-4b and H-5a or H-5b). ^{13}C NMR ($CDCl_3$): δ 29.43 (bac-CH_3), 95.31 (bac-CH), 114.26 (C-6'a or C-6'b), 114.36 (C-6'a or C-6'b), 123.38 (C-5'a or C-5'b), 123.50 (C-5'a or C-5'b), 127.04 (bac-*ortho*), 127.29 (C-4'a or C-4'b), 127.50 (C-4'a or C-4'b), 128.08 (bac-*meta*), 130.31 (bac-*para*), 133.39 (C-5a and C-5b), 134.03 (C-3'a or C-3'b), 134.23 (C-3'a or C-3'b), 134.89 (C-4a and C-4b), 181.38 and 190.20 (bac-CO).

2-Phenylpyridine, 201.

201 was obtained commercially (EGA-Chemie). ^1H NMR ($CDCl_3$): δ 7.20 (m, 1H, H-5), 7.40 (t, 1H, H-4'), 7.47 (t, 2H, H-3' and H-5'), 7.72 (m, 2H, H-3 and H-4), 7.99 (d, 2H, H-2' and H-6'), 8.69 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 120.56 (C-3), 122.08 (C-5), 126.90 (C-2' and C-6'), 128.73 (C-3' and C-5'), 128.93 (C-4'), 136.72 (C-4), 149.67 (C-6).



201

(i) REACTION WITH RHODIUM TRICHLORIDE

201 and rhodium trichloride trihydrate were reacted in glycerol to give $[Rh(\mathbf{201}\text{-}H)_2Cl]_2$, as previously reported.[50] Mp >300°C. Anal. Calcd for $C_{44}H_{32}N_4Cl_2Rh_2.{}^1/_3CH_2Cl_2$: C, 57.68; H, 3.57; N, 6.08; Found: C, 57.73; H, 3.61; N, 5.98%. ^{1}H NMR ($CDCl_3$): δ 5.95 (d, 1H, H-3'), 6.65 (t, 1H, H-4'), 6.78 (t, 1H, H-5), 6.82 (t, 1H, H-5'), 7.55 (d, 1H, H-6'), 7.81 (t, 1H, H-4), 7.87 (d, 1H, H-3), 9.22 (d, 1H, H-6).

Ligand exchange of $[Rh(\mathbf{201}\text{-}H)_2Cl]_2$ with sodium acetylacetonate gave $Rh(\mathbf{201}\text{-}H)_2(acac)$ in 82% yield. Mp >300°C. Anal. Calcd for $C_{27}H_{23}N_2O_2Rh.{}^1/_2H_2O$: C, 62.43; H, 4.66; N, 5.39; Found: C, 62.50; H, 4.61; N, 5.41%. ^{1}H NMR ($CDCl_3$): δ 1.87 (s, 6H, acac-CH_3), 5.22 (s, 1H, acac-CH), 6.29 (d, 2H, H-3'), 6.77 (t, 2H, H-4'), 6.89 (t, 2H, H-5'), 7.20 (t, 2H, H-5), 7.59 (d, 2H, H-6'), 7.84 (t, 2H, H-4), 7.87 (d, 2H, H-3), 8.51 (d, 2H, H-6). ^{13}C NMR ($CDCl_3$): δ 29.05 (acac-CH_3), 98.05 (acac-CH), 118.69 (C-3), 121.63 (C-5), 121.95 (C-5'), 123.56 (C-6'), 128.93 (C-4'), 133.73 (C-3'), 136.90 (C-4), 148.99 (C-6), 187.33 (acac-CO).

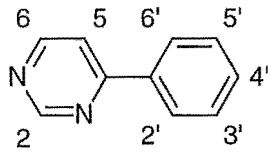
Ligand exchange of $[Rh(\mathbf{201}\text{-}H)_2Cl]_2$ with sodium dibenzoylmethanate gave $Rh(\mathbf{201}\text{-}H)_2(dbm)$ in quantitative yield. Vapour diffusion of pentane into a chloroform solution of the complex gave the analytical sample. Mp 286-287°C. Anal. Calcd for $C_{37}H_{27}N_2O_2Rh.{}^1/_2CHCl_3$: C, 64.88; H, 3.99; N, 4.04; Found: C, 64.52; H, 4.31; N, 4.08%. ^{1}H NMR ($CDCl_3$): δ 6.40 (d, 2H, H-3'), 6.55 (s, 1H, dbm-CH), 6.82 (t, 2H, H-4'), 6.94 (t, 2H, H-5'), 7.10 (t, 2H, H-5), 7.29 (t, 4H, dbm-*meta*), 7.36 (t, 2H, dbm-*para*), 7.63 (d, 2H, H-6'), 7.78 (t, 2H, H-4), 7.79 (d, 4H, dbm-*ortho*), 7.87 (d, 2H, H-3), 8.59 (d, 2H, H-6). ^{13}C NMR ($CDCl_3$): δ 92.49 (dbm-CH), 118.57 (C-3), 121.65 (C-5), 121.79 (C-5'), 123.43 (C-6'), 127.09 (dbm-*ortho*), 127.97 (dbm-*meta*), 128.70 (C-4'), 130.00 (dbm-*para*), 133.89 (C-3'), 136.93 (C-4), 149.06 (C-6), 182.35 (dbm-CO).

Ligand exchange of $[Rh(\mathbf{201}\text{-}H)_2Cl]_2$ with sodium benzoylacetonate gave $Rh(\mathbf{201}\text{-}H)_2(bac)$ in 71% yield. Vapour diffusion of pentane into a chloroform solution

of the complex gave the analytical sample. Mp 270-271°C. Anal. Calcd for $C_{32}H_{25}N_2O_2Rh.^3/_2H_2O$: C, 64.11; H, 4.71; N, 4.67; Found: C, 64.05; H, 4.48; N, 4.89%. ^1H NMR ($CDCl_3$): δ 2.01 (bac-CH_3), 5.88 (s, 1H, bac-CH), 6.34 (d, 1H, H-3'a or H-3'b), 6.36 (d, 1H, H-3'a or H-3'b), 6.80 (t, 2H, H-4'a and H-4'b), 6.92 (m, H-5'a and H-5'b), 7.14 (t, 1H, H-5a or H-5b), 7.17 (t, 1H, H-5a or H-5b), 7.25 (t, 2H, bac-*meta*), 7.32 (t, 1H, bac-*para*), 7.62 (d, 2H, H-6'a and H-6'b), 7.70 (d, 2H, bac-*ortho*), 7.81 (m, 2H, H-4a and H-4b), 7.87 (m, 2H, H-3a and H-3b), 8.54 (d, 1H, H-6a or H-6b), 8.56 (d, 1H, H-6a or H-6b). ^{13}C NMR ($CDCl_3$): δ 29.53 (bac-CH_3), 95.15 (bac-CH), 118.57 (C-3a or C-3b), 118.66 (C-3a or C-3b), 121.61 (C-5a or C-5b), 121.68 (C-5a or C-5b), 121.77 (C-5'a or C-5'b), 121.97 (C-5'a or C-5'b), 123.38 (C-6'a or C-6'b), 123.59 (C-6'a or C-6'b), 126.98 (bac-*ortho*), 127.89 (bac-*meta*), 128.66 (C-4'a or C-4'b), 128.89 (C-4'a or C-4'b), 129.87 (bac-*para*), 133.69 (C-3'a or C-3'b), 133.87 (C-3'a or C-3'b), 136.93 (C-4a and C-4b), 148.92 (C-6a or C-6b), 148.98 (C-6a or C-6b), 180.54 and 189.14 (bac-CO).

4-Phenylpyrimidine , 202.

202 was obtained commercially (EGA Chemie). ^1H NMR ($CDCl_3$): δ 7.53 (m, 3H, H-3', H-4' and H-5'), 7.73 (d, 1H, H-5), 8.10 (m, 2H, H-2' and H-6'), 8.78 (d, 1H, H-6), 9.28 (s, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 116.88 (C-5), 127.01 (C-2' and C-6'), 128.92 (C-3' and C-5'), 130.98 (C-4'), 136.36 (C-1'), 157.33 (C-6), 158.97 (C-2), 163.74 (C-4).



202

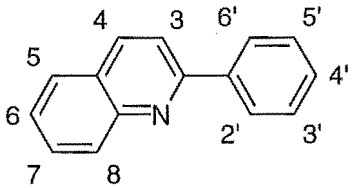
(i) REACTION WITH RHODIUM TRICHLORIDE

A solution of rhodium trichloride trihydrate (204 mg, 0.77 mmol) and **202** (387 mg, 2.47 mmol) in 2-methoxyethanol (20 cm^3) was heated under reflux for two days. The resultant suspension was stripped of solvent under reduced pressure and the oily residue taken up in dichloromethane (10 cm^3). Addition of ether gave

mer-Rh(**202**)$_3$Cl$_3$ as a yellow powder in 73% yield. Recrystallisation from dichloromethane/ether gave the analytical sample as orange crystals. Mp 216°C. Anal. Calcd for $C_{30}H_{24}N_6Cl_3Rh$: C, 53.16; H, 3.57; N, 12.40; Cl, 15.69; Found: C, 53.19; H, 3.50; N, 12.60; Cl, 15.99%. ^{1}H NMR ($CDCl_3$): δ 7.55 (t, 2H, H-3'-*cis* and H-5'-*cis*), 7.58 (t, 4H, H-3'-*trans* and H-5'-*trans*), 7.59 (t, 2H, H-4'-*trans*), 7.62 (t, 1H, H-4'-*cis*), 7.82 (d, 1H, H-6-*cis*), 7.85 (d, 2H, H-6-*trans*), 8.14 (d, 4H, H-2'-*trans* and H-6'-*trans*), 8.16 (H-2'-*cis* and H-6'-*cis*), 8.97 (d, 1H, H-5-*cis*), 9.40 (s, 2H, H-2-*trans*), 9.42 (d, 2H, H-5-*trans*), 9.46 (s, 1H, H-2-*cis*). ^{13}C NMR ($CDCl_3$): δ 116.74 (C-6-*trans*), 117.26 (C-6-*cis*), 127.82 (C-2'-*trans* and C-6'-*trans*), 127.90 (C-2'-*cis* and C-6'-*cis*), 129.32 (C-3'-*trans* and C-5'-*trans*), 129.45 (C-3'-*cis* and C-5'-*cis*), 132.63 (C-4'-*trans*), 133.19 (C-4'-*cis*), 133.86 (C-1'-*cis*), 134.46 (C-1'-*trans*), 160.27 (C-5-*cis*), 162.18 (C-2-*cis*), 162.72 (C-2-*trans* and C-5-*trans*), 165.21 (C-4-*trans*), 165.77 (C-4-*cis*).

2-Phenylquinoline, 203.

203 was obtained commercially (Aldrich). ^{1}H NMR ($CDCl_3$): δ 7.48 (t, 1H, H-4'), 7.52 (t, 2H, H-3' and H-5'), 7.56 (t, 1H, H-6), 7.74 (t, 1H, H-7), 7.85 (d, 1H, H-5), 7.89 (d, 1H, H-3), 8.17 (d, 2H, H-2' and H-6'), 8.19 (d, 1H, H-8), 8.24 (d, 1H, H-4). ^{1}H NMR (CD_3CN): δ 7.56 (t, 1H, H-4'), 7.63 (t, 2H, H-3' and H-5'), 7.65 (t, 1H, H-6), 7.83 (t, 1H, H-7), 8.00 (d, 1H, H-5), 8.10 (d, 1H, H-3), 8.16 (d, 1H, H-8), 8.31 (d, 2H, H-2' and H-6'), 8.42 (d, 1H, H-4). ^{13}C NMR ($CDCl_3$): δ 118.94 (C-3), 126.22 (C-6), 127.12 (C4a), 127.41 (C-5), 127.53 (C-2' and C-6'), 128.80 (C-3' and C-5'), 129.27 (C-4'), 129.60 (C-7), 129.69 (C-8), 136.72 (C-4), 139.63 (C-1'), 148.24 (C-8a), 157.31 (C-2).



203

(i) REACTION WITH RHODIUM TRICHLORIDE

A solution of **203** (498 mg, 2.43 mmol) and rhodium trichloride trihydrate (202 mg, 0.77 mmol) in 2-methoxyethanol (20 cm^3) was stirred at room temperature for one

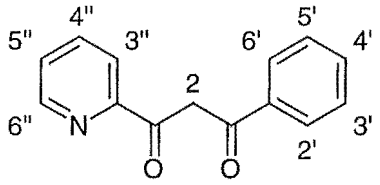
day then stirred under reflux for one day after which the resultant suspension was cooled to room temperature and refrigerated overnight. The precipitate was filtered off, washed with 2-methoxyethanol (20 cm^3) and dried under reduced pressure to give 299 mg of a yellow/green powder. Vapour diffusion of ether into an acetonitrile solution of this powder followed by manual separation gave Rh(**203**-H)$_2$Cl.$^1/_4$CH$_3$CN, **204**, as orange crystals suitable for single crystal X-ray structure determination and [Rh(**203**-H)(CH$_3$CN)Cl$_2$]$_x$, **205**, as amorphous yellow blocks. **204**: Mp 303-306°C (dec.). Anal. Calcd for $C_{30}H_{20}N_2ClRh.^1/_4CH_3CN$: C, 65.76; H, 3.75; N, 5.66; Cl, 6.36; Found: C, 66.23; H, 3.81; N, 5.88; Cl, 6.37%. ^{1}H NMR (CD$_3$CN, 23°C): δ 6.22 (d, 1H, H-3'), 6.77 (t, 1H, H-4'), 7.07 (t, 1H, H-5'), 7.76 (t, 1H, H-6), 7.89 (t, 1H, H-7), 7.96 (d, 1H, H-6'), 8.13 (d, 1H, H-5), 8.31 (d, 1H, H-3), 8.65 (d, 1H, H-4). ^{1}H NMR (CD$_3$CN, 60°C): δ 6.23 (d, 1H, H-3'), 6.77 (t, 1H, H-4'), 7.07 (t, 1H, H-5'), 7.75 (t, 1H, H-6), 7.87 (t, 1H, H-7), 7.96 (d, 1H, H-6'), 8.12 (d, 1H, H-5), 8.30 (d, 1H, H-3), 8.63 (d, 1H, H-4), 9.48 (br m, 1H, H-8). ^{13}C NMR (CD$_3$CN): complex not sufficiently soluble to obtain data. **205**: Mp >300°C. Anal. Calcd for [$C_{15}H_{10}NCl_2Rh.CH_3CN$]$_x$: C, 48.72; H, 3.13; N, 6.68; Cl, 16.92; Found: C, 48.48; H, 2.83; N, 6.50; Cl, 17.09%. ^{1}H NMR (CD$_3$CN): δ 7.28 (t, 1H, H-5'), 7.39 (t, 1H, H-4'), 7.74 (t, 1H, H-6), 7.97 (d, 1H, H-6'), 8.00 (d, 1H, H-5), 8.00 (t, 1H, H-7), 8.03 (d, 1H, H-3'), 8.14 (d, 1H, H-3), 8.44 (d, 1H, H-4), 9.52 (d, 1H, H-8). ^{13}C NMR (CD$_3$CN): complex not sufficiently soluble to obtain data.

Ligand exchange of the mixture of **204** and **205** (41.5 mg) with sodium acetylacetonate gave 36.8 mg of a yellow powder. Vapour diffusion of pentane into a chloroform solution of this powder gave Rh(**203**-H)$_2$(acac), **206**, as orange blocks,. Mp 265°C (dec.). Anal. Calcd for $C_{35}H_{27}N_2O_2Rh$: C, 68.86; H, 4.46; N, 4.59; Found: C, 68.46; H, 4.25; N, 4.56%. ^{1}H NMR (CDCl$_3$): δ 1.55 (s, 6H, acac-CH$_3$), 4.65 (s, 1H, acac-CH), 6.54 (d, 2H, H-3'), 6.70 (t, 2H, H-4'), 7.01 (t, 2H, H-5'), 7.47 (t, 2H, H-6), 7.50 (t, 2H, H-7), 7.81 (m, 2H, H-5), 7.87 (d, 2H, H-6'), 8.09 (d, 2H, H-3), 8.29 (d, 2H, H-4), 8.67 (m, 2H, H-8). ^{13}C NMR (CDCl$_3$): δ 28.74 (acac-CH$_3$), 98.02 (acac-CH), 116.90 (C-3), 122.19 (C-5'), 125.54 (C-6'), 126.11 (C-6), 127.25 (C-8), 127.48 (C-5), 128.49 (C-4'), 130.07 (C-7), 136.14 (C-3'), 137.77 (C-4), 187.43 (acac-CO). Vapour diffusion of pentane into the supernatant from these orange crystals gave

Rh(**203**-H)(acac)$_2$, **207**, as an amorphous yellow solid. Anal. Calcd for $C_{25}H_{24}NO_4Rh$: C, 59.42; H, 4.79; N, 2.77; Found: C, 59.75; H, 4.54; N, 2.81%. ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 3H, $acac_a$-CH_3), 1.82 (s, 3H, $acac_b$-CH_3), 2.19 (s, 6H, $acac_a$-CH_3 and $acac_b$-CH_3), 5.17 (s, 1H, $acac_b$-CH), 5.45 (s, 1H, $acac_a$-CH), 7.23 (t, 1H, H-5'), 7.27 (t, 1H, H-4'), 7.52 (t, 1H, H-6), 7.60 (m, 1H, H-3'), 7.71 (t, 1H, H-7), 7.75 (d, 1H, H-5), 7.87 (m, 1H, H-6'), 8.00 (d, 1H, H-3), 8.17 (d, 1H, H-4), 9.18 (d, 1H, H-8). ^{13}C NMR ($CDCl_3$): δ 26.63 ($acac_b$-CH_3), 27.03 ($acac_a$-CH_3 or $acac_b$-CH_3), 27.55 ($acac_a$-CH_3), 28.91 ($acac_a$-CH_3 or $acac_b$-CH_3), 98.62 ($acac_b$-CH), 99.77 ($acac_a$-CH), 116.86 (C-3), 123.50 (C-5'), 125.62 (C-6'), 126.26 (C-6), 126.43 (C-8), 127.69 (C-5), 129.20 (C-4'), 130.64 (C-7), 134.47 (C-3'), 138.25 (C-4).

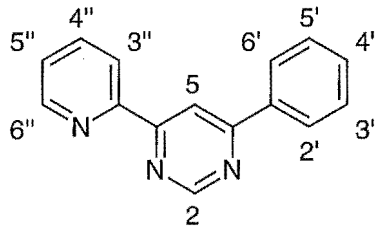
4-Phenyl-6-(2-pyridyl)pyrimidine, 210.

Methanol (2.5 cm^3) was added to a stirred mixture of sodium chips (0.96 g, 42 mmol) in ether (100 cm^3) under a nitrogen atmosphere. To the resultant mixture were added dropwise a solution of ethyl picolinate (5.4 cm^3, 40 mmol) in ether (40 cm^3) followed by a solution of acetophenone (9.4 cm^3, 80 mmol) in ether (40 cm^3). The resultant suspension was then stirred under reflux for two hours after which it was cooled to room temperature and the yellow solid filtered off and washed with ether (50 cm^3) then air dried. This solid was then added, with stirring, to a solution of acetic acid (40 cm^3) in water (50 cm^3) and ice (125 g) to give a suspension which was filtered and the cream coloured solid washed with water (300 cm^3) to give 1-phenyl-3-(2-pyridyl)-1,3-propanedione, **211**, in 85% yield. Mp 85-85.5°C (lit.[117] 87-87.5°C). IR (KBr pellet): ν_{max} 1601, 1552, 1478, 1459, 1423, 1310, 775, 751, 709, 689, 611 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.44 (t, 1H, H-5''), 7.49 (t, 2H, H-3' and H-5'), 7.54 (t, 1H, H-4'), 7.59 (s, 2H, H-2), 7.87 (t, 1H, H-4''), 8.08 (d, 2H, H-2' and H-6'), 8.17 (d, 1H, H-3''), 8.71 (d, 1H, H-6''). ^{13}C NMR ($CDCl_3$): δ 93.51 (C-2), 122.10 (C-3''), 126.33 (C-5''), 127.45 (C-2' and C-6'), 128.60 (C-3' and C-5'), 132.62 (C-4'), 135.26 (C-1'), 137.02 (C-4''), 149.24 (C-6''), 152.47 (C-2''), 183.64 (C-1 or C-3), 186.26 (C-1 or C-3).



211

210 was prepared by the reaction of **211** with formamide as previously reported.[116] Mp 100-105°C (lit.[116] 102-103°C). Calcd for $C_{15}H_{11}N_3$: M^+, 233.0953; Found (EI): M^+, 233.0953. IR (KBr pellet): ν_{max} 1593, 1576, 1520, 1454, 1371, 748, 687, 631 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44 (t, 1H, H-5"), 7.54 (m, 3H, H-3', H-4' and H-5'), 7.91 (t, 1H, H-4"), 8.25 (m, H-2' and H-6'), 8.54 (d, 1H, H-3"), 8.77 (d, 1H, H-6"), 8.84 (s, 1H, H-5), 9.34 (s, 1H, H-2). ^1H NMR (d_6-DMSO): δ 7.69 (m, 3H, H-3', H-4' and H-5'), 7.70 (t, 1H, H-5"), 8.14 (t, 1H, H-4"), 8.36 (m, 2H, H-2' and H-6'), 8.58 (d, 1H, H-3"), 8.90 (d, 1H, H-6"), 8.91 (s, 1H, H-5), 9.44 (s, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 113.04 (C-5), 121.79 (C-3"), 125.39 (C-5"), 127.29 (C-2' and C-6'), 128.92 (C-3' and C-5'), 130.97 (C-4'), 136.79 (C-1'), 137.21 (C-4"), 149.48 (C-6"), 153.99 (C-2"), 158.77 (C-2), 163.24 (C-4 or C-6), 165.08 (C-4 or C-6). ^{13}C NMR (d_6-DMSO): δ 112.16 (C-5), 121.48 (C-3"), 126.13 (C-5"), 127.14 (C-2' and C-6'), 129.21 (C-3' and C-5'), 131.36 (C-4'), 136.22 (C-1'), 137.83 (C-4"), 149.85 (C-6"), 153.17 (C-2"), 158.97 (C-2), 162.98 (C-4 or C-6), 164.10 (C-4 or C-6).



210

(i) REACTION WITH PALLADIUM ACETATE

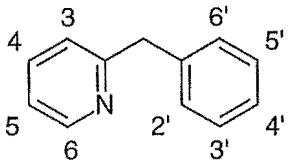
Palladium acetate (19.6 mg, 0.087 mmol) was dissolved in benzene (5 cm^3) and the resultant solution filtered into a solution of **210** (20.3 mg, 0.087 mmol) in benzene (2.5 cm^3). The mixture was briefly stirred then allowed to stand at room temperature for several days after which the resultant suspension was filtered and the yellow solid washed with benzene (25 cm^3) then ether (15 cm^3) to give Pd(**210**)$(OAc)_2$, **212**, in 79%

yield. Mp 228°C (dec.). Anal. Calcd for $C_{19}H_{17}N_3O_4Pd$: C, 49.85; H, 3.74; N, 9.18; Found: C, 49.57; 3.83; N, 9.20%. IR (KBr pellet): ν_{max} 1632, 1609, 1526, 1464, 1389, 1364, 1319, 735, 689 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.09 (s, 3H, CH_3COO), 2.18 (s, 3H, CH_3COO), 7.28 (t, 1H, H-5''), 7.56 (t, 2H, H-3' and H-5'), 7.64 (t, 1H, H-4'), 7.94 (d, 1H, H-6''), 8.37 (t, 1H, H-4''), 8.39 (d, 2H, H-2' and H-6'), 8.54 (s, 1H, H-2), 9.06 (s, 1H, H-5), 9.30 (d, 1H, H-3''). ^{13}C NMR ($CDCl_3$): δ 23.20 and 23.27 (CH_3COO), 113.97 (C-5), 126.26 (C-3''), 127.49 (C-5''), 128.53 (C-2' and C-6'), 129.45 (C-3' and C-5'), 130.17 (C-1'), 133.67 (C-4'), 141.61 (C-4''), 149.92 (C-6''), 153.71 (C-2''), 157.45 (C-2), 167.39 (C-4 or C-6), 178.54 (C-4 or C-6), 200.58 and 205.86 (CH_3COO).

Ligand exchange of **212** with excess lithium chloride in acetone/water (60/40, v/v) gave Pd(**210**)Cl_2, **220**, in 84% yield. Mp >300°C. Anal. Calcd for $C_{15}H_{11}N_3Cl_2Pd$: C, 43.88; H, 2.70; N, 10.23; Cl, 17.27; Found: C, 43.82; H, 2.48; N, 10.09; Cl, 16.53%. IR (KBr pellet): ν_{max} 1607, 1524, 1489, 1464, 1439, 1389, 791, 752, 735, 689 cm^{-1}. This complex was insoluble in common NMR solvents.

2-Benzylpyridine, 221.

221 was obtained commercially (Aldrich). ^1H NMR ($CDCl_3$): δ 4.16 (s, 2H, $-CH_2-$), 7.11 (m, 2H, H-3 and H-5), 7.27 (m, 4H, H-2', H-3', H-5' and H-6'), 7.31 (t, 1H, H-4'), 7.57 (t, 1H, H-4), 8.55 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ44.63 ($-CH_2-$), 121.12 (C-5), 122.98 (C-3), 126.26 (C-4'), 128.47 (C-2' and C-6'), 129.00 (C-3' and C-5'), 136.40 (C-4'), 139.40 (C-1'), 149.23 (C-6), 160.89 (C-2).



221

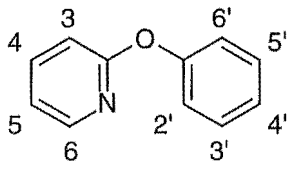
(i) REACTION WITH RHODIUM TRICHLORIDE

A solution of **221** (184 mg, 1.09 mmol) and anhydrous rhodium trichloride (102 mg, 0.49 mmol) in anhydrous ethanol (20 cm^3) was stirred under reflux in a nitrogen atmosphere for one day after which the solution was filtered and the filtrate stripped of

solvent to give *fac*-Rh(**221**)$_3$Cl$_3$ as an oil in quantitative yield. ^{1}H NMR ($CDCl_3$): δ 4.64 (s, 2H, -CH_2-), 7.33 (m, 1H, H-4'), 7.38 (m, 4H, H-2', H-3', H-5' and H-6'), 7.52 (d, 1H, H-3), 7.70 (t, 1H, H-5), 8.21 (t, 1H, H-4), 8.73 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 39.13 (-CH_2-), 124.15 (C-5), 126.66 (C-3), 127.81 (C-4'), 129.28 (C-3' and C-5'), 129.39 (C-2' and C-6'), 134.79 (C-1'), 141.16 (C-6), 144.88 (C-4), 156.84 (C-2).

2-Phenoxypyridine, 232.

232 was prepared by the reaction of phenol with 2-bromopyridine in the presence of anhydrous potassium carbonate, as previously reported.[135] The product, obtained as white crystals from the ether extracts of the steam distillate of the basified reaction mixture, was used without further purification. Mp 41.5-43.5°C. Calcd for $C_{11}H_9NO$: M^+, 171.0684; Found (EI): M^+, 171.0687. IR (KBr pellet): ν_{max} 1588, 1569, 1488, 1466, 1426, 1284, 1264, 1240, 1201, 1160, 876, 775, 694 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.90 (d, 1H, H-3), 6.99 (t, 1H, H-5), 7.14 (d, 2H, H-2' and H-6'), 7.20 (t, 1H, H-4'), 7.40 (t, 2H, H-3' and H-5'), 7.68 (t, 1H, H-4), 8.20 (d, 1H, H-6). ^{1}H NMR (d_6-DMSO): δ 7.12 (d, 1H, H-3), 7.22 (t, 1H, H-5), 7.23 (d, 2H, H-2' and H-6'), 7.30 (t, 1H, H-4'), 7.51 (t, 2H, H-3' and H-5'), 7.94 (t, 1H, H-4), 8.25 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 111.47 (C-3), 118.41 (C-5), 121.12 (C-2' and C-6'), 124.62 (C-4'), 129.65 (C-3' and C-5'), 139.36 (C-4), 147.74 (C-6), 154.11 (C-1'), 163.72 (C-2). ^{13}C NMR (d_6-DMSO): δ 111.58 (C-3), 119.08 (C-5), 121.25 (C-2' and C-6'), 124.53 (C-4'), 129.74 (C-3' and C-5'), 140.20 (C-4), 147.51 (C-6), 153.98 (C-1'), 163.11 (C-2).



232

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

232 was reacted with one equivalent of lithium tetrachloropalladate to give Pd(**232**)$_2$Cl$_2$, **234**, in 87% yield. Vapour diffusion of petroleum ether into a chloroform solution of the complex gave the analytical sample as orange crystals suitable for single crystal X-ray structure determination. Mp >300°C. Anal. Calcd for

$C_{22}H_{18}N_2O_2Cl_2Pd.^1/_7CHCl_3$: C, 49.55; H, 3.41; N, 5.22; Cl, 16.04; Found: C, 49.62; H, 3.22; N, 5.24; Cl, 15.96%. IR (KBr pellet): ν_{max} 1605, 1574, 1488, 1472, 1437, 1295, 1280, 1263, 1197, 1154, 770, 760, 695 cm^{-1}. ^1H NMR ($CDCl_3$, 23°C): δ 6.60 (d, 1H, H-3), 7.04 (t, 1H, H-5), 7.23-7.47 (br m, 5H, H-2', H-3', H-4', H-5' and H-6'), 7.64 (t, 1H, H-4), 8.65 (d, 1H, H-6). ^1H NMR ($CDCl_3$, 53°C): δ 6.60 (d, 1H, H-3), 7.01 (t, 1H, H-5), 7.25 (t, 1H, H-4'), 7.32 (d, 2H, H-2' and H-6'), 7.40 (t, 2H, H-3' and H-5'), 7.61 (t, 1H, H-4), 8.65 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$, 23°C): δ 111.90 (C-3), 119.15 (C-5), 121.33 (C-2' and C-6'), 125.95 (C-4'), 130.20 (C-3' and C-5'), 140.47 (C-4), 151.19 (C-6), 154.02 (C-1'), 164.52 (C-2). ^{13}C NMR ($CDCl_3$, 53°C): δ 111.98 (C-3), 119.11 (C-5), 121.36 (C-2' and C-6'), 125.90 (C-4'), 130.19 (C-3' and C-5'), 140.89 (C-4), 151.40 (C-6).

(ii) REACTION WITH PALLADIUM ACETATE

An acetic acid (15 cm^3) solution of **232** (186 mg, 1.09 mmol) and palladium acetate (204 mg, 0.91 mmol) was stirred at room temperature for one day. The resultant pale yellow precipitate was filtered off and washed with water (50 cm^3), methanol (20 cm^3) then ether (20 cm^3) to give [Pd(**232**-H)OAc]$_2$, **235**, in 69% yield. Vapour diffusion of petroleum ether into a chloroform solution of the complex gave the analytical sample. Mp 226-228°C. Anal. Calcd for $C_{26}H_{22}N_2O_2Pd_2$: C, 46.52; H, 3.03; N, 4.17; Found: C, 46.24; H, 3.10; N, 4.14%. IR (KBr pellet): ν_{max} 1610, 1583, 1568, 1478, 1454, 1422, 1327, 1298, 1181, 775, 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.12 (s, 3H, *CH*$_3$COO), 6.62 (d, 1H, H-6'), 6.63 (t, 1H, H-5), 6.66 (t, 1H, H-4'), 6.82 (d, 1H, H-3'), 6.86 (t, 1H, H-5'), 6.88 (d, 1H, H-3), 7.55 (t, 1H, 4), 8.02 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 24.53 (*C*H$_3$COO), 114.29 (C-3), 115.18 (C-6'), 117.80 (C-5), 123.06 (C-4'), 124.90 (C-5'), 134.08 (C-3'), 139.80 (C-4), 148.82 (C-6), 149.30 (C-1'), 157.30 (C-2), 181.16 (CH$_3$*C*OO).

Ligand exchange of **235** with excess lithium chloride in acetone/water (60/40, v/v) gave [Pd(**232**-H)Cl]$_2$, **236**, in 69% yield. Mp >300°C. Anal. Calcd for $C_{22}H_{16}N_2O_2Cl_2Pd_2$: C, 42.34; H, 2.58; N, 4.49: Cl, 11.36; Found: C, 42.49; H, 2.23; N, 4.27; Cl, 11.27%. IR (KBr pellet): ν_{max} 1610, 1577, 1480, 1454, 1437, 1424, 1313,

1302, 1184, 770, 749, 731 cm^{-1}. This complex was insoluble in common NMR solvents.

Ligand exchange of **236** with sodium acetylacetonate gave Pd(**232**-H)(acac), **237**, in 43% yield. Mp 133-135°C. Anal. Calcd for $C_{16}H_{15}NO_3Pd$: C, 51.15; H, 4.02; N, 3.73; Found: C, 50.89; H, 3.72; N, 3.84%. IR (KBr pellet): ν_{max} 1612, 1595, 1577, 1528, 1479, 1441, 1426, 1406, 1314, 1300, 761, 749, 732 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.04 (s, 3H, acac-CH_3), 2.09 (s, 3H, acac-CH_3), 5.42 (s, 1H, acac-CH), 6.98 (d, 1H, H-6'), 7.06 (t, 1H, H-4'), 7.08 (t, 1H, H-5), 7.12 (t, 1H, H-5'), 7.22 (d, 1H, H-3), 7.62 (d, 1H, H-3'), 7.82 (t, 1H, H-4), 8.81 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 27.58 and 27.95 (acac-CH_3), 100.39 (acac-CH), 114.91 (C-3), 115.47 (C-6'), 118.53 (C-5), 123.68 (C-4'), 125.65 (C-5'), 133.83 (C-3'), 140.27 (C-4), 148.22 (C-6), 187.02 and 188.12 (acac-CO).

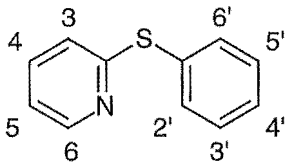
(iii) REACTION WITH BUTYLLITHIUM

A solution of **232** (250 mg, 1.46 mmol) in ether was degassed by passing a stream of nitrogen bubbles through it for 5 minutes, after which time n-butyllithium (1.6mol dm^{-3} in hexane, 1.0 cm^3) was added and the resultant solution was stirred at room temperature under a nitrogen atmosphere. After 12 hours a sample (1.0 cm^3) was withdrawn, quenched with D_2O and the ^1H NMR spectrum of the evaporated organic phase recorded to give a spectrum largely indistinguishable from that of unreacted **232**. An additional aliquot of n-butyllithium (1.6 mol dm^{-3} in hexane, 1.0 cm^3) was added to the reaction mixture and the resultant solution stirred for a further 24 hours at room temperature under a nitrogen atmosphere, after which time the solution was quenched with D_2O (0.5 cm^3). The reaction mixture was then washed with water (10 cm^3) and the aqueous phase extracted with ether (10 cm^3). The organic phases were combined and washed with saturated aqueous sodium chloride solution (10 cm^3) then dried over anhydrous magnesium sulfate and the solvent removed to give 6-butyl-2-phenoxypyridine, **240**, as a yellow oil. Yield 60%. Calcd for $C_{15}H_{17}NO$: M^+, 227.1310; Found (EI): M^+, 227.1308. ^1H NMR ($CDCl_3$): δ 0.91 (t, 3H, -$CH_2CH_2CH_2CH_3$), 1.35 (sxt, 2H, -$CH_2CH_2CH_2CH_3$), 1.67 (qnt, 2H,

-$CH_2CH_2CH_2CH_3$), 2.70 (t, 2H, -$CH_2CH_2CH_2CH_3$), 6.57 (d, 1H, H-3), 6.86 (d, 1H, H-5), 7.13 (d, 2H, H-2' and H-6'), 7.20 (t, 1H, H-4'), 7.38 (t, 2H, H-3' and H-5'), 7.55 (t, 1H, H-4). ^{13}C NMR ($CDCl_3$): δ 13.88 (-$CH_2CH_2CH_2CH_3$), 22.35 (-$CH_2CH_2CH_2CH_3$), 31.58 (-$CH_2CH_2CH_2CH_3$), 37.48 (-$CH_2CH_2CH_2CH_3$), 117.40 (C-5), 120.65 (C-2' and C-6'), 124.23 (C-4'), 129.27 (C-6), 129.57 (C-3' and C-5'), 139.51 (C-4), 154.64 (C-1'), 161.75 (C-2).

2-Phenylthiopyridine, 233

233 was prepared by the reaction of thiophenol with 2-chloropyridine in the presence of triethylamine as previously described.[140] Calcd for $C_{11}H_9NS$: M^+, 187.0456; Found (EI): M^+, 187.0454. ^1H NMR ($CDCl_3$): δ 6.87 (d, 1H, H-3), 6.98 (t, 1H, H-5), 7.41 (m, 3H, H-3', H-4' and H-5'), 7.42 (t, 1H, H-4), 7.59 (d, 2H, H-2' and H-6'), 8.41 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 119.77 (C-5), 121.20 (C-3), 128.98 (C-4'), 129.52 (C-3' and C-5'), 130.88 (C-1'), 134.83 (C-2' and C-6'), 136.61 (C-4), 149.44 (C-6), 161.40 (C-2).



233

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

233 was reacted with one equivalent of lithium tetrachloropalladate to give Pd(**233**)$_2$Cl$_2$ in 75% yield. Mp 265-266.5°C (dec.). Anal. Calcd for $C_{22}H_{18}N_2S_2Cl_2Pd$: C, 47.88; H, 3.29; N, 5.08; Cl, 12.85; Found: C, 47.18; H, 3.18; N, 5.20; Cl, 13.22%. IR (KBr pellet): ν_{max} 1589, 1558, 1474, 1452, 1421, 1275, 1094, 760, 702, 691 cm^{-1}.

(ii) REACTION WITH PALLADIUM ACETATE

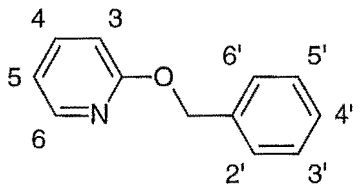
232 and palladium acetate were reacted according to method B to give [Pd(**232**-H)Cl]$_2$, **238**, in 47% yield. IR (KBr pellet): ν_{max} 1587, 1551, 1458, 1431,

1421, 1157, 1020, 762, 746 cm^{-1}. This complex was insoluble in common NMR solvents.

Ligand exchange of **238** with thallium acetylacetonate followed by the vapour diffusion of pentane into a chloroform solution of the complex gave Pd(**232**-H)(acac), **239**, in 20% yield. Mp 199-200°C (dec.). Anal. Calcd for $C_{16}H_{15}NO_2SPd$: C, 49.05; H, 3.86; N, 3.58; Found: C, 48.81; H, 4.02; N, 3.55%. IR (KBr pellet): ν_{max} 1592, 1559, 1511, 1420, 1394, 774, 745, 612 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.00 (s, 3H, acac-CH_3), 2.05 (s, 3H, acac-CH_3), 5.42 (s, 1H, acac-CH), 7.01 (t, 1H, H-5'), 7.07 (t, 1H, H-4'), 7.17 (t, 1H, H-5), 7.30 (d, 1H, H-6'), 7.44 (d, 1H, H-3'), 7.66 (t, 1H, H-4), 7.73 (d, 1H, H-3), 8.81 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 27.52 and 27.98 (acac-CH_3), 100.34 (acac-CH), 121.56 (C-5), 124.64 (C-5'), 125.82 (C-3), 126.02 (C-4'), 126.83 (C-6'), 131.75 (C-2'), 135.75 (C-3'), 137.32 (C-4), 145.63 (C-1'), 153.77 (C-6), 158.68 (C-2), 186.57 and 187.92 (acac-CO).

2-Phenylmethoxypyridine, 241.

241 was prepared by a phase-transfer reaction between benzyl alcohol and 2-chloropyridine in toluene in the presence of potassium hydroxide and a catalyst as previously reported.[165] The catalyst employed in the literature preparation was 18-crown-6, however, given the cost of this reagent, tetrabutylammonium hydroxide was used for this preparation to give, after reduced pressure distillation, the ligand in 56% yield (lit.[165] 80%). Calcd for $C_{12}H_{11}NO$: M^+, 185.0841; Found (EI): M^+, 185.0840. ^1H NMR ($CDCl_3$): δ 5.38 (s, 2H, -CH_2-), 6.81 (d, 1H, H-3), 6.88 (t, 1H, H-5), 7.31 (t, 1H, H-4'), 7.38 (t, 2H, H-3' and H-5'), 7.47 (d, 2H, H-2' and H-6'), 7.58 (t, 1H, H-4), 8.18 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ67.49 (-CH_2-), 111.31 (C-5), 116.89 (C-3), 127.80 (C-4'), 127.93 (C-2' and C-6'), 128.44 (C-3' and C-5'), 137.31 (C-1'), 138.61 (C-4), 146.79 (C-6).



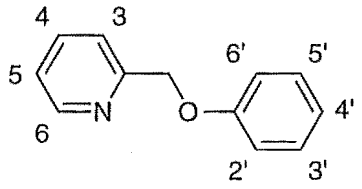
241

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

Lithium tetrachloropalladate was reacted with two equivalents of **241** without stirring to give Pd(**241**)$_2$Cl$_2$, **246**, in 71% yield. Mp 196.5-197°C (dec.). Anal. Calcd for $C_{24}H_{22}N_2O_2Cl_2Pd$: C, 52.63; H, 4.05; N, 5.11; Cl, 12.94; Found: C, 52.42; H, 4.10; N, 5.11; Cl, 13.14%. IR (KBr pellet): ν_{max} 1607, 1576, 1489, 1445, 1317, 1300, 1043, 1016, 988, 775, 750, 733, 692 cm^{-1}. ^{1}H NMR ($CDCl_3$, 23°C): δ 5.34 (br s, 2H, -CH_2-), 6.72 (d, 1H, H-3), 6.95 (t, 1H, H-5), 7.34 (br s, 3H, H-3', H-4' and H-5'), 7.65 (t, 1H, H-4), 7.72 (br s, H-2' and H-6'), 8.57 (br s, 1H, H-6). ^{1}H NMR ($CDCl_3$, 53°C): δ 5.38 (s, 2H, -CH_2-), 6.71 (d, 1H, H-3), 6.94 (t, 1H, H-5), 7.29 (t, 1H, H-4'), 7.36 (t, 2H, H-3' and H-5'), 7.63 (t, 1H, H-4), 7.71 (d, 2H, H-2' and H-6'), 8.57 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$, 23°C): δ 71.54 (-CH_2-), 109.01 (C-5), 118.13 (C-3), 127.41 (C-4'), 128.21 (C-2' and C-6'), 128.66 (C-3' and C-5'), 135.07 (C-1'), 140.89 (C-4), 151.21 (C-6), 163.75 (C-2).

2-Phenoxymethylpyridine, 242.

Phenol (4.63 g, 49.2 mmol) and 2-chloromethylpyridine hydrochloride (8.74 g, 53.3 mmol) were reacted under phase-transfer conditions in benzene (15 cm^3) and aqueous sodium hydroxide (10 mol dm^{-3}, 17 cm^3, 170 mmol) with tetrabutylammonium hydroxide as catalyst. The mixture was stirred under reflux for one day then cooled. The crude reaction mixture was extracted with ether/water (50/50, v/v, 30 cm^3) then ether (2 x 20 cm^3) and the combined organic extracts dried over anhydrous sodium sulfate. Removal of solvent, followed by distillation at reduced pressure, gave **242**. Yield 62%. Calcd for $C_{12}H_{11}NO$: M^+, 185.0841; Found (EI): M^+, 185.0842. ^{1}H NMR ($CDCl_3$): δ 5.21 (s, 2H, -CH_2-), 6.97 (t, 1H, H-4'), 6.99 (d, 2H, H-2' and H-6'), 7.22 (t, 1H, H-5), 7.30 (t, 2H, H-3' and H-5'), 7.53 (d, 1H, H-3), 7.71 (t, 1H, H-4), 8.60 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 70.45 (-CH_2-), 114.75 (C-2' and C-6'), 121.09 (C-4'), 121.23 (C-3), 122.56 (C-5), 129.49 (C-3' and C-5'), 136.81 (C-4), 149.14 (C-6).



242

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

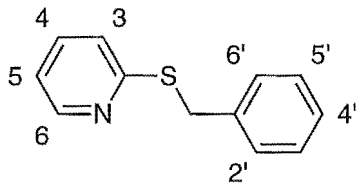
Lithium tetrachloropalladate was reacted with two equivalents of **242** without stirring to give Pd(**242**)$_2$Cl$_2$, **247**, in 77% yield. Diffusion of petroleum ether into a chloroform solution of the complex gave the analytical sample as yellow crystals suitable for single crystal X-ray structure determination. Mp 209.5-210°C (dec.). Anal. Calcd for $C_{24}H_{22}N_2O_2Cl_2Pd$: C, 52.63; H, 4.05; N, 5.11; Cl, 12.94; Found: C, 52.35; H, 3.84; N, 5.04; Cl, 13.40%. IR (KBr pellet): ν_{max} 1599, 1587, 1497, 1441, 1261, 1242, 1227, 1080, 1063, 775, 752, 691 cm^{-1}. ^{1}H NMR ($CDCl_3$, 23°C): δ 6.34 (s, 2H, -CH_2-), 6.92-7.27 (br m, 5H, H-2', H-3', H-4', H-5' and H-6'), 7.32 (br s, 1H, H-5), 7.64 (d, 1H, H-3), 7.79 (t, 1H, H-4), 8.96 (br d, 1H, H-6). ^{1}H NMR ($CDCl_3$, 53°C): δ 6.33 (s, 2H, -CH_2-), 6.98 (t, 1H, H-4'), 7.12 (d, 2H, H-2' and H-6'), 7.27 (t, 2H, H-3' and H-5'), 7.29 (t, 1H, H-5), 7.63 (d, 1H, H-3), 7.76 (t, 1H, H-4), 8.95 (br s, 1H, H-6). ^{13}C NMR ($CDCl_3$, 23°C): δ 69.82 (-CH_2-), 114.93 (C-2' and C-6'), 121.70 (C-4'), 123.92 (C-3 and C-5), 129.79 (C-3' and C-5'), 138.90 (C-4), 152.11 (C-6).

(ii) REACTION WITH POTASSIUM TETRABROMOPALLADATE

A solution of potassium tetrabromopalladate (102 mg, 0.20 mmol) in methanol (30 cm^3) was heated to boiling then filtered. To the filtrate was added **242** (85 mg, 0.46 mmol) and the solution was left to stand overnight. The resultant crystals were filtered and washed with methanol (10 cm^3) then ether (20 cm^3) to give Pd(**242**)$_2$Br$_2$, **249**, in 46% yield. Mp 238.5-239.5°C (dec.). Anal. Calcd for $C_{24}H_{22}N_2O_2Br_2Pd$: C, 45.28; H, 3.48; N, 4.40; Br, 25.10; Found: C, 44.05; H, 3.51; N, 4.47; Br, 25.24%. IR (KBr pellet): ν_{max} 1611, 1597, 1587, 1574, 1496, 1439, 1373, 1240, 1225, 1171, 1080, 1061, 773, 752, 691 cm^{-1}.

2-[(Phenylmethyl)thio]pyridine, 243.

2-Chloropyridine (14.1 g, 124 mmol) and benzyl mercaptan (17.0 g, 137 mmol) were reacted under phase-transfer conditions in toluene (150 cm^3) with potassium hydroxide (17.1 g, 305 mmol) and tetrabutylammonium hydroxide (1.39 g, 5.4 mmol) as catalyst. The mixture was stirred under reflux for 2 hours after which it was cooled and poured into ice/water (100 cm^3). The organic phase was separated and the aqueous phase extracted with toluene (50 cm^3). The organic extracts were combined and washed with saturated aqueous potassium chloride solution (2 x 100 cm^3) then dried over anhydrous sodium sulfate. Removal of solvent followed by distillation at reduced pressure gave **243**. Yield 25%. Calcd for $C_{12}H_{11}NS$: M^+, 201.0612; Found (EI): M^+, 201.0614. ^1H NMR ($CDCl_3$): δ 4.44 (s, 2H, -SCH_2-), 6.98 (t, 1H, H-5), 7.15 (d, 1H, H-3), 7.22 (t, 1H, H-4'), 7.29 (t, 2H, H-3' and H-5'), 7.40 (d, 2H, H-2' and H-6'), 7.45 (t, 1H, H-4), 8.45 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 34.36 (-SCH_2-), 119.53 (C-5), 122.02 (C-3), 127.04 (C-4'), 128.42 (C-2' and C-6'), 128.90 (C-3' and C-5'), 135.91 (C-4), 137.89 (C-1'), 149.34 (C-6).



243

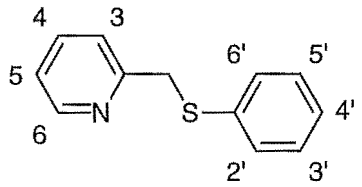
(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

Lithium tetrachloropalladate was reacted with two equivalents of **243** to give Pd(**243**)$_2Cl_2$ in 82% yield. Mp 217°C. Anal. Calcd for $C_{24}H_{22}N_2S_2Cl_2Pd$: C, 49.71; H, 3.82; N, 4.83; S, 11.06; Cl, 12.23; Found: C, 49.60; H, 3.99; N, 4.72; S, 10.91; Cl, 12.24%. IR (KBr pellet): ν_{max} 1585, 1558, 1495, 1456, 1437, 1425, 1161, 1148, 1101, 766, 729, 704 cm^{-1}. This complex is insoluble in common NMR solvents.

2-[(Phenylthio)methyl]pyridine, 244.

244 was prepared by the reaction of freshly prepared sodium thiophenoxide and 2-chloromethylpyridine hydrochloride as previously reported.[170] Calcd for $C_{12}H_{11}NS$:

M^+, 201.0612; Found (EI): M^+, 201.0613. ^{1}H NMR ($CDCl_3$): δ 4.26 (s, 2H, -CH_2S-), 7.13 (t, 1H, H-5), 7.16 (t, 1H, H-4'), 7.24 (t, 2H, H-3' and H-5'), 7.31 (d, 1H, H-3), 7.33 (d, 2H, H-2' and H-6'), 7.59 (t, 1H, H-4), 8.54 (d, 1H, H-6). ^{1}H NMR (d_6-DMSO): δ 4.43 (s, 2H, -CH_2S-), 7.25 (t, 1H, H-4'), 7.34 (t, 1H, H-5), 7.37 (t, 2H, H-3' and H-5'), 7.46 (d, 2H, H-2' and H-6'), 7.52 (d, 1H, H-3), 7.81 (t, 1H, H-4), 8.58 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 40.38 (-CH_2S-), 121.90 (C-5), 122.80 (C-3), 126.18 (C-4'), 128.72 (C-3' and C-5'), 129.45 (C-2' and C-6'), 135.69 (C-2), 136.47 (C-4), 149.18 (C-6), 157.53 (C-1'). ^{13}C NMR (d_6-DMSO): δ 38.71 (-CH_2S-), 122.30 (C-5), 123.07 (C-3), 125.85 (C-4'), 128.16 (C-3' and C-5'), 129.01 (C-2' and C-6'), 136.13 (C-2), 136.82 (C-4), 149.07 (C-6), 157.55 (C-1').



244

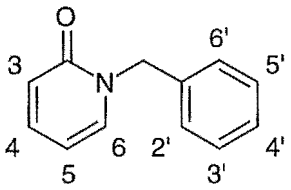
(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

Lithium tetrachloropalladate was reacted with two equivalents of **244** to give Pd(**244**)Cl_2, **248**, in 88% yield. Mp 262.5°C. Anal. Calcd for $C_{12}H_{11}NSCl_2Pd$: C, 38.07; H, 2.93; N, 3.70; S, 8.47; Cl, 18.73; Found: C, 38.02; H, 2.91; N, 3.88; S, 8.45; Cl, 18.68%. Calcd for $C_{12}H_{11}NSCl_2Pd$: M^+, 343.9340; Found (FAB): M^+, 343.9356. IR (KBr pellet): ν_{max} 1605, 1475, 1439, 1400, 1277, 1165, 781, 739, 685 cm^{-1}. ^{1}H NMR (d_6-DMSO): δ 4.92 (d, 1H, -CH_2-Ha), 5.47 (d, 1H, -CH_2-Hb), 7.59 (br m, 3H, H-3', H-4' and H-5'), 7.67 (t, 1H, H-5), 7.88 (d, 1H, H-3), 7.92 (d, 2H, H-2' and H-6'), 8.20 (t, 1H, H-4), 9.21 (d, 1H, H-6). ^{13}C NMR (d_6-DMSO): δ 46.07 (-CH_2-), 124.37 (C-3), 124.67 (C-5), 129.39 (C-1'), 130.20 (C-3' and C-5'), 130.29 (C-2' and C-6'), 130.67 (C-4'), 140.68 (C-4), 151.45 (C-6), 163.21 (C-2).

1-Benzyl-2(1*H*)-pyridone, 245.

In an attempt to prepare **241**, 2-hydroxypyridine (1.01 g, 10.6 mmol) and benzyl chloride (1.32 g, 10.4 mmol), were reacted under phase-transfer conditions in benzene

(15 cm^3) and aqueous sodium hydroxide (10 mol dm^{-3}, 1.5 cm^3, 15 mmol) with tetrabutylammonium hydroxide as catalyst. The mixture was stirred under reflux for one day then cooled. The crude reaction mixture was extracted with ether/water (50/50, v/v, 10 cm^3) then ether (10 cm^3) and the combined organic extracts dried over anhydrous sodium sulfate. Removal of solvent, followed by recrystallisation of the crude residue from petroleum ether and drying under reduced pressure gave **245**. Yield 52%. Mp 67.5-69°C (lit. [162] 75°C). Calcd for $C_{12}H_{11}NO$: M^+, 185.0841; Found (EI): M^+, 185.0838. IR (KBr pellet): ν_{max} 1659, 1582, 1540, 1458, 764, 734, 698 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.14 (s, 2H, $-CH_2-$), 6.13 (t, 1H, H-5), 6.61 (d, 1H, H-3), 7.26 (d, 1H, H-6), 7.30 (t, 1H, H-4), 7.32 (m, 5H, H-2', H-3', H-4', H-5' and H-6'). ^{13}C NMR ($CDCl_3$): δ 51.74 ($-CH_2-$), 106.12 (C-5), 121.12 (C-3), 127.89 (C-4'), 128.01 (C-2' and C-6'), 128.77 (C-3' and C-5'), 136.27 (C-1'), 137.15 (C-4), 139.32 (C-6), 162.57 (C-2).

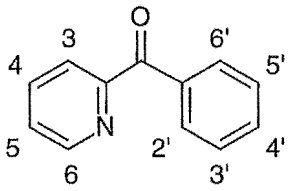


245

2-Benzoylpyridine, 301.

301 was obtained commercially (EGA-Chemie). IR (KBr pellet): ν_{max} 1669, 1579, 1448, 1322, 1302, 1283, 943, 778, 750, 732, 705, 650 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50 (t, 3H, H-5, H-3' and H-5'), 7.60 (t, 1H, H-4'), 7.92 (t, 1H, H-4), 8.05 (d, 1H, H-3), 8.07 (d, 2H, H-2' and H-6'), 8.74 (d, 1H, H-6). ^1H NMR (d_6-DMSO): δ 7.64 (t, 2H, H-3' and H-5'), 7.77 (t, 2H, H-5 and H-4'), 8.06 (d, 2H, H-2' and H-6'), 8.09 (d, 1H, H-3), 8.17 (t, H-4), 8.82 (d, 1H, H-6). ^1H NMR (CD_3CN): δ 7.57 (t, 2H, H-3' and H-5'), 7.64 (t, 1H, H-5), 7.70 (t, 1H, H-4'), 8.05 (m, 2H, H-3 and H-4), 8.06 (d, 2H, H-2' and H-6'), 8.74 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 124.55 (C-3), 126.11 (C-5), 128.10 (C-3' and C-5'), 130.91 (C-2' and C-6'), 132.87 (C-4'), 136.18 (C-1'), 137.00 (C-4), 148.49 (C-6), 155.01 (C-2), 193.86 (-CO-). ^{13}C NMR (d_6-DMSO): δ 124.32 (C-3), 126.91 (C-5), 128.38 (C-3' and C-5'), 130.74 (C-2' and C-6'), 133.17 (C-4'), 136.12 (C-1'), 137.83 (C-4), 148.73 (C-6), 154.61 (C-2), 193.64 (-CO-). ^{13}C NMR (CD_3CN):

δ 125.14 (C-3), 127.44 (C-5), 129.04 (C-3' and C-5'), 131.68 (C-2' and C-6'), 133.77 (C-4'), 137.60 (C-1'), 138.30 (C-4), 149.51 (C-6), 156.03 (C-2), 194.94 (-CO-).



301

(i) REACTION WITH RHODIUM TRICHLORIDE IN 2-METHOXYETHANOL

A solution of **301** (243 mg, 1.33 mmol) and rhodium trichloride trihydrate (100 mg, 0.38 mmol) in 2-methoxyethanol (10 cm^3) was stirred at room temperature for four days. The resultant dark red suspension was then stirred under reflux for one day during which time a yellow precipitate formed. The suspension was cooled to room temperature, refrigerated then filtered and the solid dried under reduced pressure to give Rh(**301**-H)(**301**-*N,O*)Cl_2, **308**, in 75% yield. Mp >300°C. Anal. Calcd for $C_{24}H_{17}N_2O_2Cl_2Rh$: C, 53.46; H, 3.18; N, 5.20; Cl, 13.15; Found: C, 53.44; H, 3.43; N, 5.27; Cl, 13.46%. IR (KBr pellet): ν_{max} 1676, 1612, 1587, 1574, 1446, 1328, 1306, 1287, 1260, 766, 753, 702, 688 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.30 (t, 1H, H-5'a), 7.45 (t, 1H, H-4'a), 7.60 (t, 1H, H-5a), 7.69 (t, 2H, H-3'b and H-5'b), 7.73 (t, 1H, H-5b), 7.82 (t, 1H, H-4'b), 7.89 (d, 1H, H-3'a), 7.99 (d, 1H, H-6'a), 8.05 (t, 1H, H-4a), 8.08 (t, 1H, H-4b), 8.09 (d, 2H, H-2'b and H-6'b), 8.19 (d, 1H, H-3b), 8.33 (d, 1H, H-3a), 8.99 (d, 1H, H-6b), 9.70 (d, 1H, H-6a). ^1H NMR (d_6-DMSO): δ 7.40 (t, 1H, H-5'a), 7.57 (t, 1H, H-4'a), 7.87 (d, 1H, H-6'a), 7.88 (t, 2H, H-3'b and H-5'b), 7.90 (d, 1H, H-3'a), 8.03 (t, 2H, H-5a and H-4'b), 8.16 (t, 1H, H-5b), 8.26 (d, 2H, H-2'b and H-6'b), 8.35 (d, 1H, H-3a), 8.42 (t, 1H, H-4a), 8.46 (t, 1H, H-4b), 8.53 (d, 1H, H-3b), 8.88 (d, 1H, H-6b), 9.63 (d, 1H, H-6a). ^{13}C NMR (d_6-DMSO): δ 124.09 (C-5'a), 125.91 (C-3a), 127.52 (C-5a), 128.03 (C-6'a), 129.55 (C-3'b and C-5'b), 130.69 (C-2'b and C-6'b), 130.83 (C-5b), 131.14 (C-4'a), 133.60 (C-3b), 135.08 (C-4'b), 139.95 (C-3'a), 140.22 (C-4a and C-4b), 153.65 (C-6a), 155.33 (C-6b), 187.76 (-COa-), 201.51 (-COb-). Quaternary signals observed but not assigned 139.24, 153.43, 155.22, 156.53 and 156.90.

Diffusion of pentane into a dimethyl sulfoxide/chloroform solution of **308** gave Rh(**301**-H)$(DMSO)_2Cl_2$, **309**, as yellow crystals suitable for single crystal X-ray structure determination. Mp >300°C. Anal. Calcd for $C_{16}H_{20}NO_3S_2Cl_2.{}^1/_2(CH_3)_2SO$: C, 37.03; H, 4.20; N, 2.54; Found: C, 37.27; H, 4.03; N, 2.51%.

Ligand exchange of **308** with thallium acetylacetonate for five days followed by the vapour diffusion of ether into a dichloromethane solution of the complex gave Rh(**301**-H)(**301**-*N*)(acac)Cl, **310**, in 22% yield. Mp 211-215°C (dec.). Calcd for $C_{29}H_{24}N_2O_4ClRh$: $(M\text{-}Cl)^+$, 567.0791; Found (FAB): 567.0788. IR (KBr pellet): ν_{max} 1651, 1597, 1576, 1518, 1439, 1387, 1310, 1286, 984, 932, 793, 775, 750, 692 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.78 (s, 3H, acac-CH_3), 2.01 (s, 3H, acac-CH_3), 5.09 (s, 1H, acac-CH), 6.92 (d, 1H, H-3'a), 7.08 (d, 1H, H-3b), 7.12 (t, 1H, H-5b), 7.14 (t, 1H, H-4'a), 7.18 (t, 1H, H-5'a), 7.32 (t, 1H, H-4'b), 7.39 (t, 2H, H-3'b and H-5'b), 7.43 (t, 1H, H-5a), 7.71 (t, 1H, H-4b), 7.78 (d, 1H, H-6b), 7.92 (d, 2H, H-2'b and H-6'b), 7.93 (d, 1H, H-6'a), 7.94 (t, 1H, H-4a), 8.14 (d, 1H, H-3a), 9.22 (d, 1H, H-6a). ^{13}C NMR ($CDCl_3$): δ 27.82 (acac-CH_3), 28.87 (acac-CH_3), 99.14 (acac-CH), 123.13 (C-5b), 123.59 (C-5'a), 123.73(C-3b), 125.36 (C-3a), 126.01 (C-5a), 127.16 (C-2'b and C-6'b), 127.70 (C-4'b), 128.09 (C-3'b and C-5'b), 129.45 (C-6a), 130.19 (C-4'a), 136.54 (C-3'a), 138.24 (C-4b), 138.28 (C-4a), 148.15 (C-6b), 152.34 (C-6a).

(ii) REACTION WITH RHODIUM TRICHLORIDE IN ETHANOL

(a) WITH SODIUM PERCHLORATE

Reaction of **301**, rhodium trichloride trihydrate and sodium perchlorate in refluxing ethanol/water (5/1, v/v) gave the yellow solid, *trans*-Rh(**301**-*N,O*)$_2Cl_2.ClO_4$, **302**, as previously reported.[188] Recrystallisation from acetonitrile/methanol gave the complex as yellow blocks suitable for single crystal X-ray structure determination. IR (KBr pellet): ν_{max} 1596, 1574, 1522, 1446, 1351, 1275, 1090, 758, 696, 687, 623 cm^{-1}. ^1H NMR (CD_3CN): δ 7.87 (t, 2H, H-3' and H-5'), 8.08 (t, 1H, H-4'), 8.29 (d, 2H, H-2' and H-6'), 8.43 (t, 1H, H-5), 8.66 (t, 1H, H-4), 8.83 (d, 1H, H-3), 9.93 (d, 1H, H-6). ^{13}C NMR (CD_3CN): complex not sufficiently soluble to obtain data.

After standing for 24 hours at room temperature, an acetonitrile solution of **302** gave a solution of *cis*-Rh(**301**-*N,O*)$_2$Cl$_2$.ClO$_4$, **304**, in quantitative yield. Vapour diffusion of ether into an acetonitrile solution of the complex gave the complex as thin yellow plates suitable for single crystal X-ray structure determination. ^{1}H NMR (CD_3CN): δ 7.75 (t, 2H, H-3' and H-5'), 7.96 (t, 1H, H-4'), 8.04 (d, 2H, H-2' and H-6'), 8.39 (t, 1H, H-5), 8.62 (t, 1H, H-4), 8.75 (d, 1H, H-3), 9.93 (d, 1H, H-6). ^{13}C NMR (CD_3CN): δ 130.55 (C-3' and C-5'), 132.15 (C-2' and C-6'), 134.57 (C-5), 137.12 (C-3), 137.76 (C-4'), 142.79 (C-4), 155.64 (C-6), 190.51 (-CO-).

Warming the yellow complex, **302**, in water gave a dark orange solid as previously reported.[188] This material was recrystallised from methanol/acetonitrile to give Rh(**301**-*N,O*)(**301**-*O*)(OH)Cl$_2$, **306**, as fine, dark red needles. IR (KBr pellet): ν_{max} 1574, 1543, 1446, 1339, 1271, 1101, 1044, 1027, 784, 777, 758, 707, 696 cm^{-1}. ^{1}H NMR (CD_3CN): δ 6.99 (d, 1H, H-H-3a), 7.43 (m, 3H, H-3'a, H-4'a and H-5'a), 7.67 (t, 1H, H-5a), 7.81 (t, 2H, H-3'b and H-5'b), 7.84 (d, 2H, H-2'a and H-6'a), 7.95 (t, 1H, H-4a), 8.00 (t, 1H, H-4'b), 8.17 (d, 1H, H-5b), 8.17 (d, 2H, H-2'b and H-6'b), 8.44 (t, 1H, H-4b), 8.64 (d, 1H, H-3b), 9.52 (d, 1H, H-6a), 9.54 (d, 1H, H-6b). ^{13}C NMR (CD_3CN): complex not sufficiently soluble to obtain data.

After standing for six days at room temperature, an acetonitrile solution of **306** gave a solution of **307** (a different isomer of Rh(**301**-*N,O*)(**301**-*O*)(OH)Cl$_2$) in quantitative yield. ^{1}H NMR (CD_3CN): δ 7.08 (d, 1H, H-3a), 7.29 (m, 3H, H-3'a , H-4'a and H-5'a), 7.51 (m, 2H, H-2'a and H-6'a), 7.68 (t, 1H, H-5a), 7.75 (t, 2H, H-3'b and H-5'b), 7.97 (t, 1H, H-4a), 8.00 (d, 2H, H-2'b and H-6'b), 8.22 (t, 1H, H-5b), 8.44 (t, 1H, H-4b), 8.57 (d, 1H, H-3b), 9.74 (d, 1H, H-6a), 9.83 (d, 1H, H-6b). ^{13}C NMR (CD_3CN): δ 125.15 (C-3a), 125.69 (C-5a), 127.37 (C-2'a and C-6'a), 128.63 (C-4'a), 128.73 (C-3'a and C-5'a), 130.47 (C-3'b and C-5'b), 131.30 (C-2'b and C-6'b), 133.26 (C-5b), 135.68 (C-3b), 136.73 (C-4'b), 140.40 (C-4a), 141.15 (C-4b), 151.18 (C-6a), 154.82 (C-6b).

(b) WITHOUT SODIUM PERCHLORATE

Reaction of 2-benzoylpyridine and rhodium trichloride trihydrate in ethanol gave an orange solid as previously reported.[188] IR (KBr pellet): ν_{max} 1594, 1575, 1539, 1509, 1445, 1349, 1272, 1036, 756, 695 cm^{-1}. This complex is insoluble in common NMR solvents.

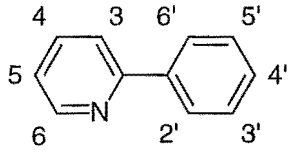
The orange solid was stirred under reflux in water for fifteen minutes to give the red solid, Rh(**301**-*N,O*)(**301**-*O*)(OH)Cl_2, **306**, as previously reported.[188] The complex was characterised by comparison of the ^1H NMR and IR spectra of the sample with that prepared above.

Stirring the red solid, **306** (80 mg), under reflux in ethanol/water (8.0 cm^3, 3/1, v/v) for three hours gave Rh(**301**-H)(**301**-*N,O*)Cl_2, **308,** (28 mg), identified by comparison of the ^1H NMR and IR spectra of the sample with that prepared above.

Direct bromination of 2-phenylpyridine, 201.

(i) REACTION WITH BROMINE AND IRON POWDER IN ACETIC ACID

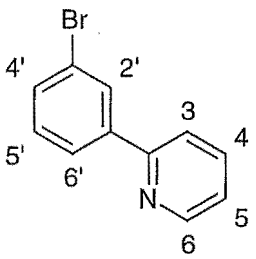
Bromine (0.08 cm^3, 3.1 mmol) was added to a stirred mixture of iron powder (19 mg, 0.3 mmol) and **201** (0.2 cm^3, 215 mg, 1.4 mmol) in acetic acid (2.5 cm^3) and the resultant mixture stirred overnight at room temperature. This gave no decolourisation of the solution, so it was stirred under reflux for three hours after which water (1 cm^3) was added and the solution refluxed overnight, after which it was poured into water (20 cm^3). The solution was decolourised by the addition of a small amount of sodium metabisulfite and then basified by the addition of sodium hydroxide. The resultant mixture was then extracted with chloroform (3 x 15 cm^3) and the combined extracts washed with sodium metabisulfite solution then dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure gave a quantitative return of **201**.



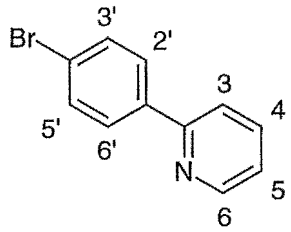
201

(ii) REACTION WITH BROMINE AND ANTIMONY PENTACHLORIDE IN DICHLOROETHANE

201 (0.2 cm^3, 215 mg, 1.4 mmol) was added to a stirred solution of antimony pentachloride (0.1 cm^3, 0.8 mmol) and bromine (0.04 cm^3, 1.6 mmol) in 1,2-dichloroethane (2 cm^3) and the resultant suspension stirred overnight at room temperature, after which it was poured into water (20 cm^3). The mixture was stirred and basified by the addition of sodium hydroxide, then transferred to a separating funnel and the organic phase separated. The aqueous phase was extracted with additional 1,2-dichloroethane (2 x 10 cm^3) and all organic extracts combined and dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure gave 226 mg of an oil. This oil was estimated by ^1H NMR to contain the following compounds: 2-(3-bromophenyl)pyridine, **407**, (trace); 2-(4-bromophenyl)pyridine, **408**, (11%) 7.89 ppm (d, H-2' and H-6'); **201** (89%).



407

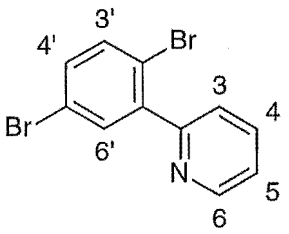


408

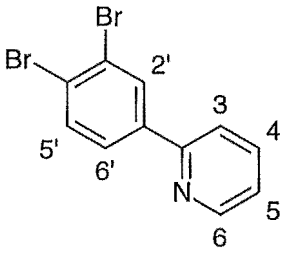
(iii) REACTION WITH BROMINE AND SILVER SULFATE IN AQUEOUS SULPHURIC ACID

Bromine (0.08 cm^3, 3.1 mmol) was added to a solution of **201** (0.2 cm^3, 215 mg, 1.4 mmol) and silver sulfate (725 mg, 2.3 mmol) in aqueous sulfuric acid (16 mol dm^{-3}, 2.5 cm^3) and the resultant suspension left to stand overnight at room temperature after which it was poured into water (15 cm^3). The precipitate was filtered off and the filtrate

basified by the addition of sodium hydroxide, then extracted with chloroform (3 x 20 cm^3) and the combined extracts dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give 87 mg of an oil. This oil was estimated by ^1H NMR to contain the following compounds: 2-(2,5-dibromophenyl)pyridine, **409**, (26%) 7.39 (d, H-4'); **408** (36%) 7.61 ppm (d, H-3' and H-5'); **201** (12%) 7.99 (d, H-2' and H-6'); **407** (16%) 8.18 (s, H-2'); 2-(3,4-dibromophenyl)pyridine, **410**, (10%) 8.30 (s, H-2').



409



410

(iv) REACTION WITH POTASSIUM BROMATE IN SULFURIC ACID

201 (0.2 cm^3, 215 mg, 1.4 mmol) was added to a solution of potassium bromate (240 mg, 1.4 mmol) in aqueous sulfuric acid (9 mol dm^{-3}, 3 cm^3) and the mixture was stirred overnight at room temperature, the flask shielded from light with aluminium foil. The solution was poured, with stirring, into water (20 cm^3) and basified by the addition of sodium hydroxide, then extracted with chloroform (3 x 10 cm^3). The combined organic extracts were then dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure to give 272 mg of an oil. This oil was estimated by ^1H NMR to contain the following compounds: **408** (24%) 7.61 ppm (d, H-3' and H-5'); **201** (39%) 7.99 (d, H-2' and H-6'); **407** (18%) 8.18 (s, H-2'); **410** (5%) 8.30 (s, H-2'); **409** (<5%, estimated due to signal overlap).

This mixture was subjected to radial chromatography, eluting with an increasing gradient of chloroform in petroleum ether to give a pure sample of **410**. Calcd for $C_{11}H_7N^{79}Br^{81}Br$ ($C_{11}H_7N^{79}Br_2$, $C_{11}H_7N^{81}Br_2$): M^+, 312.8927 (310.8946, 314.8907); Found (EI): M^+, 312.8921 (310.8935, 314.8906). ^1H NMR ($CDCl_3$): δ 7.30 (t, 1H, H-5), 7.70 (d, 1H, H-3), 7.72 (d, 1H, H-5'), 7.79 (t, 1H, H-4), 7.80 (d, 1H, H-6'), 8.30 (s, 1H, H-2'), 8.70 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 120.40 (C-5), 122.92 (C-3), 126.74

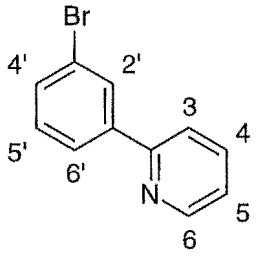
(C-6'), 132.02 (C-2'), 133.89 (C-5'), 137.06 (C-4), 149.87 (C-6). ^{1}H NMR analysis of another mixed fraction facilitated the partial characterisation of two further compounds: **408** (31% of mixture, estimated by ^{1}H NMR). ^{1}H NMR ($CDCl_3$): δ 7.27 (t, 1H, H-5), 7.61 (d, 2H, H-3' and H-5'), 7.72 (d, 1H, H-3), 7.78 (t, 1H, H-4), 7.89 (d, 2H, H-2' and H-6'), 8.72 (d, 1H, H-6). **409** (69%). ^{1}H NMR ($CDCl_3$): δ 7.33 (t, 1H, H-5), 7.39 (d, H-4'), 7.54 (d, 1H, H-3'), 7.61 (d, 1H, H-3), 7.70 (s, 1H, H-6'), 7.79 (t, 1H, H-4), 8.72 (d, 1H, H-6).

2-(3-Bromophenyl)pyridine, 407.

(i) *VIA* DIAZOTISATION OF 3-BROMOANILINE WITH NITROUS ACID

3-Bromoaniline (25.0 g, 145 mmol) was dissolved in a solution of hydrochloric acid (10 mol dm^{-3}, 60 cm^3) and water (400 cm^3) and the resultant solution cooled to 3°C by the addition of dry ice. A chilled solution of sodium nitrite (11.02 g, 160 mmol) in water (60 cm^3) was added in 2 cm^3 portions to the solution prepared above with the temperature of the mixture maintained below 5°C. The resultant solution was transferred to a chilled dropping funnel and added slowly, with stirring, to pyridine (250 cm^3) at room temperature. Throughout the addition dry ice was added periodically to the solution of diazonium salt to prevent thermal decomposition. The resultant mixture was then stirred overnight at room temperature, after which it was made strongly alkaline by the addition of sodium hydroxide and left to stand for two days. The mixture was steam distilled and the distillate collected when cloudy, after all of the pyridine had been removed. The distillate (1200 cm^3) was extracted with ether (combined volume 600 cm^3) and the extracts washed with water (250 cm^3), then dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure to give 750 mg of a yellow oil. This oil was estimated by ^{1}H NMR to contain the following compounds: 3-bromoaniline (9%) 6.58 ppm (d, H-6); 3-bromophenol (7%) 7.60 (s, H-2); **407** (51%) 8.18 (s, H-2'); 3-nitrobromobenzene (1%) 8.40 (s, H-2); 3-(3-bromophenyl)pyridine (14%) 8.82 (s, H-2); 4-(3-bromophenyl)pyridine (<10%, estimated due to signal overlap).

This mixture was subjected to radial chromatography, eluting with a gradient of chloroform in petroleum ether, to give **407** (320 mg) as an oil contaminated by 3-bromoaniline (estimated by ^{1}H NMR 22% of the mixture) as well as a small quantity (2.7 mg) of the pure compound. Calcd for $C_{11}H_8N^{79}Br$ ($C_{11}H_8N^{81}Br$): M^+, 232.9840 (234.9820); Found (EI): M^+, 232.9838 (234.9821). ^{1}H NMR ($CDCl_3$): δ 7.27 (t, 1H, H-5), 7.35 (t, 1H, H-5'), 7.55 (d, 1H, H-4'), 7.71 (d, 1H, H-3), 7.78 (t, 1H, H-4), 7.92 (d, 1H, H-6'), 8.18 (s, 1H, H-2'), 8.71 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 120.60 (C-3), 122.67 (C-5), 123.02 (C-3'), 125.38 (C-6'), 130.00 (C-2'), 130.23 (C-5'), 131.84 (C-4'), 136.93 (C-4), 141.32 (C-1'), 149.72 (C-6), 155.80 (C-2).



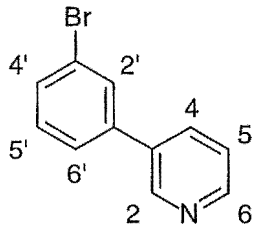
407

(i) *VIA* DIAZOTISATION OF 3-BROMOANILINE WITH *ISO*-AMYL NITRITE

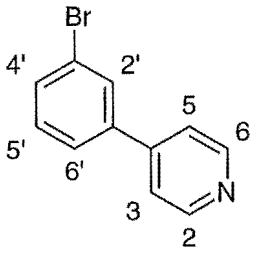
A solution of freshly distilled 3-bromoaniline (13.5 cm^3, 21 g, 120 mmol) in pyridine (125 cm^3) was treated with isoamyl nitrite (40.0 cm^3, 35 g, 300 mmol) to give, after work-up, an oil containing a mixture of **407**, 3-(3-bromophenyl)pyridine and 4-(3-bromophenyl)pyridine as previously reported.[217] The proportions of (bromophenyl)pyridines in the oil were estimated by ^{1}H NMR analysis as: **407** (42%); 3-(3-bromophenyl)pyridine (28%); 4-(3-bromophenyl)pyridine (30%).

A sample of this oil (1.50 g) was subjected to chromatography on a silica gel column, with chloroform as eluent, to give a pure sample of each of the (bromophenyl)pyridines. 3-(3-bromophenyl)pyridine (**A**). Calcd for $C_{11}H_8N^{79}Br$ ($C_{11}H_8N^{81}Br$): M^+, 232.9840 (234.9820); Found (EI): M^+, 232.9840 (234.9817). ^{1}H NMR ($CDCl_3$): δ 7.36 (t, 1H, H-5'), 7.39 (t, 1H, H-5), 7.52 (d, 1H, H-6'), 7.54 (d, 1H, H-4'), 7.73 (s, 1H, H-2'), 7.85 (d, 1H, H-4), 8.62 (d, 1H, H-6), 8.82 (s, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 123.18 (C-3'), 123.62 (C-5), 125.76 (C-6'), 130.19 (C-2'), 130.57 (C-5'), 130.62 (C-3), 131.07 (C-4'), 134.38 (C-4), 139.92 (C-1'), 148.18 (C-2), 149.04

(C-6). 4-(3-bromophenyl)pyridine (**B**). Calcd for $C_{11}H_8N^{79}Br$ ($C_{11}H_8N^{81}Br$): M^+, 232.9840 (234.9820); Found (EI): M^+, 232.9833 (234.9820). ^1H NMR ($CDCl_3$): δ 7.36 (t, 1H, H-5'), 7.48 (d, 2H, H-3 and H-5), 7.56 (d, 1H, H-6'), 7.58 (d, 1H, H-4'), 7.78 (s, 1H, H-2'), 8.68 (d, 2H, H-2 and H-6). ^{13}C NMR ($CDCl_3$): δ 121.52 (C-3 and C-5), 123.19 (C-3'), 125.57 (C-6'), 130.02 (C-2'), 130.57 (C-5'), 131.94 (C-4'), 140.16 (C-1'), 146.84 (C-4), 150.27 (C-2 and C-6).



A



B

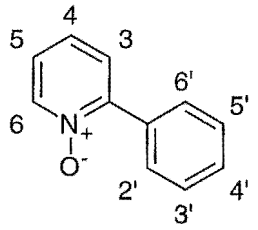
The remainder of the oil (7.34 g) was subjected to chromatography on a silica gel column, eluting with an increasing gradient of chloroform in petroleum ether (40-60°C), to give **407** (3.48 g) as a dark brown oil which was used without further purification. Yield 12% (based on 3-bromoaniline).

2-Phenylpyridine 1-oxide, 412.

Reaction of pyridine (81.0 cm^3, 1.01 mol) and freshly prepared phenyllithium [from lithium (7.35 g, 1.06 mol) and bromobenzene (52.5 cm^3, 0.50 mol)] in toluene gave **201** as previously reported.[284] Yield 26%. During the isolation of the product a small fraction (1.11 g) was collected from the initial distillation under reduced pressure which, upon standing at room temperature, solidified to give a pale yellow product which was identified as 4,4'-bipyridine by comparison of its ^1H NMR spectrum with that of an authentic sample.

Reaction of **201** with hydrogen peroxide in acetic acid gave **412**, as previously reported.[228] Mp 155-157°C (lit.[228] 157°C). ^1H NMR ($CDCl_3$): δ 7.20 (t, 1H, H-5), 7.29 (t, 1H, H-4), 7.40 (d, 1H, H-3), 7.44 (t, 2H, H-3' and H-5'), 7.46 (t, 1H, H-4'), 7.80 (d, 2H, H-2' and H-6'), 8.31 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 124.13 (C-3), 125.50

(C-5), 126.92 (C-4), 127.74 (C-2' and C-6'), 128.75 (C-3' and C-5'), 129.07 (C-4'), 139.87 (C-6).

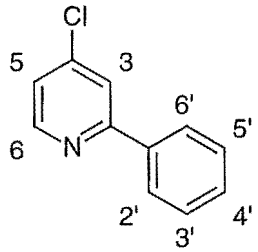


412

2-Phenyl-4-chloropyridine, 411.

Reaction of **412** with sulfuryl chloride followed by treatment with alcoholic picric acid gave the picrate of 2-phenyl-4-chloropyridine as previously reported.[226] Mp 179-182°C (lit.[226] 177-182°C).

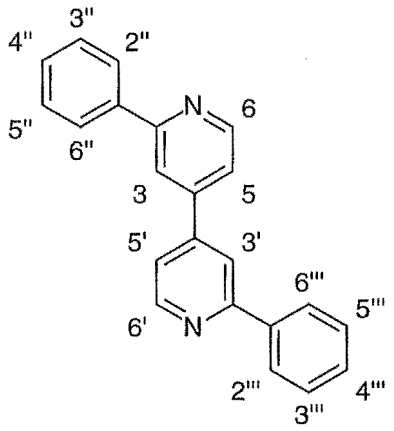
The picrate of 2-phenyl-4-chloropyridine (5.41 g, 12.9 mmol) was warmed with aqueous sodium hydroxide (1.3 mol dm^{-3}, 100 cm^3) to give a dark brown solution, which was cooled to room temperature, then diluted with water (200 cm^3). The resultant solution was extracted with ether (4 x 100 cm^3) and the combined extracts dried over anhydrous magnesium sulfate and the ether removed under reduced pressure. The residue was taken up in chloroform (100 cm^3), the solution filtered and the solvent removed under reduced pressure to give, in quantitative yield, **411** as a brown oil, which was used without further purification. Calcd for $C_{11}H_8N^{35}Cl$: M^+, 189.0345; Found (EI): M^+, 189.0344. ^1H NMR ($CDCl_3$): δ 7.22 (d, 1H, H-5), 7.42 (t, 1H, H-4'), 7.47 (t, 2H, H-3' and H-5'), 7.71 (s, 1H, H-3), 7.96 (d, 2H, H-2' and H-6'), 8.57 (d, 1H, H-6). ^{13}C NMR ($CDCl_3$): δ 120.78 (C-3), 122.21 (C-5), 126.90 (C-2' and C-6'), 128.79 (C-3' and C-5'), 129.54 (C-4'), 138.03 (C-1'), 144.65 (C-4), 150.41 (C-6), 158.90 (C-2).



411

2,2'-Diphenyl-4,4'-bipyridine, 402.

A mixture of tetraethylammonium iodide (1.03 g, 4.01 mmol), zinc powder (399 mg, 6.11 mmol) and $NiBr_2(PPh_3)_2$ (893 mg, 1.20 mmol) was placed into a flask and the flask evacuated then filled with argon, and the cycle repeated five times. THF (20 cm^3) was transferred into the flask and the resultant mixture stirred and heated at 50°C for 30 minutes, after which an argon-purged solution of **411** (703 mg, 3.71 mmol) in THF (15 cm^3) was transferred into the flask. The mixture was kept at 50°C and stirred under an argon atmosphere for 25 hours. The resultant suspension was poured into aqueous ammonia solution (2 mol dm^{-3}, 100 cm^3) and ether/benzene (50/50, v/v, 100 cm^3) was then added and the resultant mixture filtered. The solid was washed with ether/benzene (50/50, v/v, 20 cm^3), the filtrates combined and transferred into a separating funnel. The separated aqueous solution was extracted with ether/benzene (50/50, v/v, 2 x 50 cm^3) and the combined organic extracts washed with water (100 cm^3), then with saturated aqueous sodium chloride solution (100 cm^3) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue subjected to chromatography on a silica gel column, eluting with chloroform/petroleum ether (60-80°C) (1/1, v/v), to give **402** as a white solid in 47% yield. Mp 112-113.5°C. Anal. Calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08; Found: C, 85.31; H, 5.37; N, 9.10%. Calcd for $C_{22}H_{16}N_2$: M^+, 308.1314; Found (EI): M^+, 308.1313. IR (KBr pellet): ν_{max} 1591, 1531, 1389, 835, 777, 745, 725, 696 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.45 (t, 2H, H-4'' and H-4'''), 7.49 (d, 2H, H-5 and H-5'), 7.51 (t, 4H, H-3'', H-5'', H-3''' and H-5'''), 7.97 (s, 2H, H-3 and H-3'), 8.06 (d, 4H, H-2'', H-6'', H-2''' and H-6'''), 8.82 (d, 2H, H-6 and H-6'). ^{13}C NMR ($CDCl_3$): δ 118.46 (C-3 and C-3'), 119.96 (C-5 and C-5'), 127.01 (C-2'', C-6'', C-2''' and C-6'''), 128.83 (C-3'', C-5'', C-3''' and C-5'''), 129.26 (C-4'' and C-4'''), 138.96 (C-1'' and C-1'''), 146.85 (C-4 and C-4'), 150.47 (C-6 and C-6'), 158.52 (C-2 and C-2').



402

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

(a) ONE EQUIVALENT

402 was reacted with one equivalent of lithium tetrachloropalladate to give [Pd(**402**-H)Cl]$_2$ in quantitative yield. Mp >300°C. IR (KBr pellet): ν_{max} 1609, 1578, 1533, 1475, 1435, 1383, 827, 773, 739, 700 cm^{-1}.

Ligand exchange of [Pd(**402**-H)Cl]$_2$ with thallium acetylacetonate in chloroform gave Pd(**402**-H)(acac), **413**, in 22% yield. Mp >300°C. Anal. Calcd for $C_{27}H_{22}N_2O_2Pd.{}^1/_3CHCl_3$: C, 59.40; H, 4.07; N, 5.07; Found: C, 59.06; H, 3.88; N, 5.35%. Calcd for $C_{27}H_{22}N_2O_2{}^{106}Pd$: M^+, 512.0713; Found (FAB): M^+, 512.0706. IR (KBr pellet): ν_{max} 1578, 1533, 1514, 1391, 1263, 773, 735, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 3H, acac-CH_3), 2.13 (s, 3H, acac-CH_3), 5.43 (s, 1H, acac-CH), 7.15 (t, 1H, H-5''), 7.22 (t, 1H, H-4''), 7.43 (d, 1H, H-5), 7.48 (t, 1H, H-4'''), 7.52 (d, 2H, H-5' and H-6''), 7.54 (t, 2H, H-3''' and H-5'''), 7.63 (d, 1H, H-3''), 7.86 (s, 1H, H-3), 7.97 (s, 1H, H-3'), 8.07 (d, 2H, H-2''' and H-6'''), 8.85 (d, 1H, H-6), 8.87 (d, 1H, H-6'). ^{13}C NMR ($CDCl_3$): δ 28.14 and 29.69 (acac-CH_3), 100.69 (acac-CH), 116.18 (C-3), 118.31 (C-3'), 119.53 (C-5), 119.77 (C-5'), 122.95 (C-6''), 124.72 (C-5''), 127.08 (C-2''' and C-6'''), 128.94 (C-3''' and C-5'''), 129.54 (C-4'' and C-4'''), 131.50 (C-3''), 148.79 (C-6'), 150.71 (C-6).

(b) TWO EQUIVALENTS

A solution of **402** (50 mg, 0.16 mmol) and lithium tetrachloropalladate (0.39 mmol) in methanol (15 cm^3) was stirred under reflux for one day after which it was filtered and the precipitate washed with methanol (3 x 10 cm^3), acetone (5 cm^3) then ether (15 cm^3) to give $[Pd_2(\mathbf{402}\text{-}2H)Cl_2]_x$ in 95% yield. Mp >300°C. IR (KBr pellet): ν_{max} 1609, 1578, 1531, 1479, 1435, 1381, 1022, 768, 729 cm^{-1}.

Ligand exchange of $[Pd_2(\mathbf{402}\text{-}2H)Cl_2]_x$ with sodium acetylacetonate gave $Pd_2(\mathbf{402}\text{-}2H)(acac)_2$, **414**, in 54% yield. Mp >300°C. Calcd for $C_{32}H_{29}N_2O_4{}^{106}Pd{}^{108}Pd$: M^+, 719.0198; Found (FAB): M^+, 719.0206. IR (KBr pellet): ν_{max} 1611, 1578, 1533, 1512, 1394, 772 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.09 (s, 6H, acac-CH_3), 2.13 (s, 6H, acac-CH_3), 5.43 (s, 2H, acac-CH), 7.17 (t, 2H, H-5" and H-5'"), 7.22 (t, 2H, H-4" and H-4'"), 7.41 (d, 2H, H-5 and H-5'), 7.54 (d, 2H, H-6" and H-6'"), 7.65 (d, 2H, H-3" and H-3'"), 7.87 (s, 2H, 3 and H-3'), 8.93 (d, 2H, H-6 and H-6'). ^{13}C NMR ($CDCl_3$): complex not sufficiently soluble to obtain data.

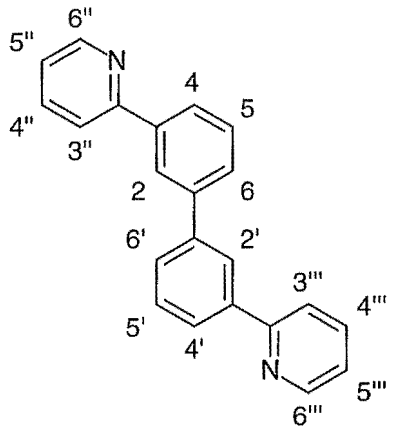
(ii) REACTION WITH PALLADIUM ACETATE

402 and two equivalents of palladium acetate were reacted according to method A to give $[Pd_2(\mathbf{402}\text{-}2H)Cl_2]_x$ in 94% yield.

3,3'-Di(2-pyridyl)biphenyl, 403.

By the method described above for the preparation of **402**, a mixture of tetraethylammonium iodide (1.05 g, 4.08 mmol), zinc powder (405 mg, 6.19 mmol) and $NiBr_2(PPh_3)_2$ (896 mg, 1.21 mmol) was used to couple **407** (926 mg, 3.96 mmol). This gave, after work-up, **403** as an oil in 50% yield. Calcd for $C_{22}H_{16}N_2$: M^+, 308.1314; Found (EI): M^+, 308.1313. ^1H NMR ($CDCl_3$): δ 7.24 (t, 2H, H-5" and H-5'"), 7.56 (t, 2H, H-5 and H-5'), 7.73 (t, 2H, H-6 and H-6'), 7.76 (t, 2H, H-4" and H-4'"), 7.80 (d, 2H, H-3" and H-3'"), 7.99 (d, 2H, H-4 and H-4'), 8.30 (s, 2H, H-2 and H-2'), 8.72 (d, 2H, H-6" and H-6'"). ^{13}C NMR ($CDCl_3$): δ 120.73 (C-3" and C-3'"), 122.19 (C-5" and C-5'"), 125.90 (C-2 and C-2'), 125.97 (C-4 and C-4'), 127.88 (C-6 and C-6'), 129.16

(C-5 and C-5'), 136.73 (C-4" and C-4'"), 139.92 (C-1 and C-1'), 141.60 (C-3 and C-3'), 149.66 (C-6" and C-6'"), 157.33 (C-2" and C-2'").



403

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

A solution of **403** (38 mg, 0.12 mmol) and lithium tetrachloropalladate (0.12 mmol) in methanol (15 cm^3) was stirred under reflux for four days after which it was filtered and the precipitate washed with methanol (3 x 10cm^3) then ether (5 cm^3) to give $[Pd_2(\mathbf{403}\text{-}H_2)Cl_2]_x$ in quantitative yield. Mp >300°C. IR (KBr pellet): ν_{max} 1605, 1564, 1481, 1458, 1425, 1016, 772 cm^{-1}.

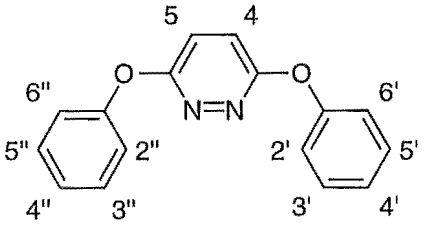
Ligand exchange of $[Pd_2(\mathbf{403}\text{-}H_2)Cl_2]_x$ with sodium acetylacetonate gave $Pd_2(\mathbf{403}\text{-}2H)(acac)_2$, **415**, in 69% yield. Mp >300°C. Anal. Calcd for $C_{32}H_{28}N_2O_4Pd_2$: C, 53.57; H, 3.93; N, 3.91; Found: C, 53.44; H, 3.99; N, 4.13%. Calcd for $C_{32}H_{28}N_2O_4{}^{106}Pd^{108}Pd$: M^+, 718.0120; Found (FAB): M^+, 718.0125. IR (KBr pellet): ν_{max} 1605, 1580, 1514, 1479, 1425, 1396, 1263, 1022, 772 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.08 (s, 6H, acac-CH_3), 2.13 (s, 6H, acac-CH_3), 5.43 (s, 2H, acac-CH), 7.19 (t, 2H, H-5" and H-5'"), 7.43 (d, 2H, 6 and H-6'), 7.64 (s, 2H, H-2 and H-2'), 7.68 (d, 2H, H-5 and H-5'), 7.75 (d, 2H, H-3" and H-3'"), 7.84 (t, 2H, H-4" and H-4'"), 8.81 (d, 2H, H-6" and H-6'"). ^{13}C NMR ($CDCl_3$): δ 27.70 and 28.13 (acac-CH_3), 100.65 (acac-CH), 118.46 (C-3" and C-3'"), 121.25 (C-2 and C-2'), 121.72 (C-5" and C-5'"), 127.74 (C-6 and C-6'), 131.71 (C-4 and C-4'), 138.46 (C-4" and C-4'"), 148.37 (C-6" and C-6'"), 187.00 and 188.21 (acac-CO).

(ii) REACTION WITH PALLADIUM ACETATE

403 and two equivalents of palladium acetate were reacted according to method A to give $[Pd_2(\mathbf{403}\text{-}H_2)Cl_2]_x$ in 68% yield.

3,6-Diphenoxypyridazine, 419.

419 was prepared by the reaction of two equivalents of sodium phenoxide with 3,6-dichloropyridazine, **442**, as previously reported.[230] Mp 141.5-142°C (lit.[230] 140-141°C). Calcd for $C_{16}H_{12}N_2O_2$: M^+, 264.0899; Found (EI): M^+, 264.0894. IR (KBr pellet): ν_{max} 1589, 1491, 1429, 1351, 1257, 1198, 1160, 872, 861, 809, 763, 736, 690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.17 (br t, 2H, H-4' and H-4"), 7.18 (br d, 4H, H-2', H-6', H-2" and H-6"), 7.19 (br s, 2H, H-4 and H-5), 7.36 (br t, 4H, H-3', H-5', H-3" and H-5"). ^1H NMR (d_6-DMSO): δ 7.30 (br d, 4H, H-2', H-6', H-2" and H-6"), 7.33 (br t, 2H, H-4' and H-4"), 7.53 (br t, 4H, H-3', H-5', H-3" and H-5"), 7.68 (br s, 2H, H-4 and H-5). ^{13}C NMR ($CDCl_3$): δ 120.97 (C-2', C-6', C-2" and C-6"), 121.75 (C-4 and C-5), 125.02 (C-4' and C-4"), 129.56 (C-3', C-5', C-3" and C-5"), 153.52 (C-1' and C-1"), 162.96 (C-3 and C-6). ^{13}C NMR (d_6-DMSO): δ 120.96 (C-2', C-6', C-2" and C-6"), 121.78 (C-4 and C-5), 125.02 (C-4' and C-4"), 129.57 (C-3', C-5', C-3" and C-5"), 153.00 (C-1' and C-1"), 162.97 (C-3 and C-6).



419

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

419 was reacted with one equivalent of lithium tetrachloropalladate to give $Pd(\mathbf{419})_2Cl_2$ in 85% yield. Recrystallisation from nitromethane gave the analytical sample. Mp 215-220°C (dec.). Anal. Calcd for $C_{32}H_{24}N_4O_4Cl_2Pd.{}^1/_2H_2O$: C, 53.76; H, 3.52; N, 7.83; Cl, 9.92; Found: C, 53.47; H, 3.38; N, 7.96; Cl, 10.10%. IR (KBr pellet): ν_{max} 1490, 1444, 1274, 1193, 1164, 847, 749, 739, 688 cm^{-1}.

(ii) REACTION WITH PALLADIUM ACETATE

419 and one equivalent of palladium acetate were reacted according to method B to give [Pd(**419**-H)Cl]$_2$ in 63% yield. IR (KBr pellet): ν_{max} 1491, 1441, 1425, 1418, 1279, 1180, 1163, 1111, 883, 764, 750, 689 cm^{-1}. This complex is insoluble in common NMR solvents.

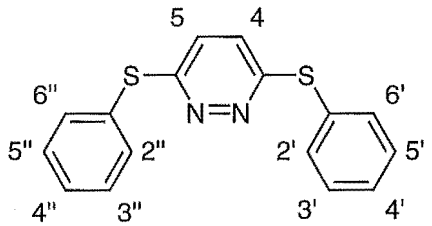
During the preparation of [Pd(**419**-H)Cl]$_2$, a sample of the corresponding μ-diacetato dipalladium complex, [Pd(**419**-H)OAc]$_2$, was isolated and characterised by NMR. ^{1}H NMR ($CDCl_3$): δ 1.68 (s, 3H, CH_3COO), 6.70 (d, 1H, H-6'), 6.83 (t, 1H, H-4'), 6.91 (t, 1H, H-5'), 6.95 (d, 3H, H-5, H-2" and H-6"), 7.11 (d, 1H, H-4), 7.16 (t, 1H, H-4"), 7.17 (d, 1H, H-3'), 7.33 (t, 2H, H-3" and H-5"). ^{13}C NMR ($CDCl_3$): δ 23.99 (CH_3COO), 114.56 (C-6'), 120.22 (C-2" and C-6"), 123.20 (C-4'), 123.26 (C-5), 124.78 (C-5'), 124.89 (C-4), 125.02 (C-4"), 129.55 (C-3" and C-5"), 134.99 (C-3'), 180.01 (CH_3COO).

Ligand exchange of [Pd(**419**-H)Cl]$_2$ with thallium acetylacetonate gave, in 87% yield, Pd(**419**-H)(acac), **455**, as pale yellow crystals suitable for single crystal X-ray structure determination. Mp 186-188°C. Anal. Calcd for $C_{21}H_{18}N_2O_4Pd$: C, 53.80; H, 3.87; N, 5.98; Found: C, 53.70; H, 3.84; N, 5.94%. IR (KBr pellet): ν_{max} 1593, 1570, 1514, 1458, 1443, 1420, 1394, 1269, 1190, 1163, 754 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H, acac-CH_3), 2.03 (s, 3H, acac-CH_3), 5.34 (s, 1H, acac-CH), 6.96 (m, 1H, H-6'), 7.07 (m, 1H, H-5'), 7.10 (m, 1H, H-4'), 7.21 (m, 1H, H-4"), 7.36 (d, 1H, H-5), 7.41 (m, 4H, H-2", H-3", H-5" and H-6"), 7.44 (d, 1H, H-4), 7.60 (m, 1H, H-3'). ^{13}C NMR ($CDCl_3$): δ 27.30 and 27.63 (acac-CH_3), 100.08 (acac-CH), 115.13 (C-6'), 120.58 (C-2'), 120.88 (C-2" and C-6"), 123.58 (C-5), 124.34 (C-5'), 125.32 (C-4"), 125.54 (C-4'), 125.60 (C-4), 129.48 (C-3" and C-5"), 134.32 (C-3'), 150.86 (C-1'), 152.87 (C-1"), 156.81 (C-3), 160.82 (C-6), 185.84 and 188.45 (acac-CO).

3,6-Bis(phenylthio)pyridazine, 423.

423 was prepared by the reaction of sodium thiophenoxide with 3,6-dichloropyridazine in ethanol as previously reported.[232] Mp 79.5-80.5°C (lit.[232]

78°C). Calcd for $C_{16}H_{12}N_2S_2$: M^+, 296.0442; Found (EI): M^+, 296.0443. IR (KBr pellet): ν_{max} 1511, 1472, 1439, 1372, 1147, 1087, 1024, 753, 704, 693 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.82 (s, 2H, H-4 and H-5), 7.40 (m, 6H, H-3', H-4', H-5', H-3", H-4" and H-5"), 7.57 (m, 4H, H-2', H-6', H-2" and H-6"). ^1H NMR (d_6-DMSO): δ 7.23 (s, 2H, H-4 and H-5), 7.55 (m, 6H, H-3', H-4', H-5', H-3", H-4" and H-5"), 7.65 (m, 4H, H-2', H-6', H-2" and H-6"). ^{13}C NMR ($CDCl_3$): δ 125.39 (C-4 and C-5), 129.26 (C-1' and C-1"), 129.55 (C-4' and C-4"), 129.79 (C-3', C-5', C-3" and C-5"), 134.95 (C-2', C-6', C-2" and C-6"), 162.20 (C-3 and C-6). ^{13}C NMR (d_6-DMSO): δ 126.60 (C-4 and C-5), 128.95 (C-1' and C-1"), 129.96 (C-4' and C-4"), 130.28 (C-3', C-5', C-3" and C-5"), 134.80 (C-2', C-6', C-2" and C-6"), 161.59 (C-3 and C-6).



423

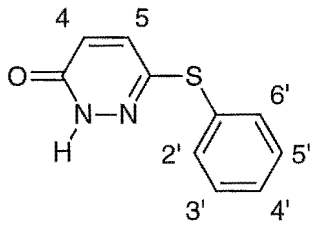
(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

423 was reacted with one equivalent of lithium tetrachloropalladate to give Pd(**423**)$_2$Cl$_2$ in 91% yield. Vapour diffusion of petroleum ether into a chloroform solution of the complex gave the analytical sample. Mp 240°C (dec.). Anal. Calcd for $C_{32}H_{24}N_4S_4Cl_2Pd$: C, 49.91; H, 3.14; N, 7.28; Cl, 9.21; Found: C, 49.69; H, 3.13; N, 7.18; Cl, 9.47%. IR (KBr pellet): ν_{max} 1474, 1440, 1395, 1154, 1022, 753, 741, 694 cm^{-1}.

6-Phenylthiopyridazin-3(2*H*)one, 444.

Triethylamine (19.0 cm^3, 136 mmol) was added dropwise to a rapidly stirred solution of 3-chloropyridazin-6(1*H*)one, **445**, (5.0 g, 38 mmol) in thiophenol (14.0 cm^3, 136 mmol). The resultant mixture was stirred at 110°C for two days after which it was allowed to cool to room temperature. The mixture was basified by the addition of aqueous sodium hydroxide (8 mol dm^{-3}, 35 cm^3) and water (20 cm^3) and the mixture extracted with benzene (4 x 50 cm^3) to remove phenyl disulfide. The basic aqueous

solution was neutralised with hydrochloric acid (3 mol dm^{-3}, 60 cm^3) and extracted with ether (4 x 100 cm^3) and the organic extracts combined and dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure followed by recrystallisation of the residue from ethanol/petroleum ether gave **444** in 47.7% yield. Mp 130-131°C. Anal. Calcd for $C_{10}H_8N_2OS$: C, 58.80; H, 3.95; N, 13.72; Found: C, 58.66; H, 3.99; N, 13.80%. Calcd for $C_{10}H_8N_2OS$: M^+, 204.0357; Found (EI): M^+, 204.0362. IR (KBr pellet): ν_{max} 1664, 1638, 1582, 1568, 1474, 1440, 1423, 1141, 998, 838, 754, 512, 480 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.85 (d, 1H, H-4), 7.06 (d, 1H, H-5), 7.38 (m, 3H, H-3', H-4' and H-5'), 7.50 (m, 2H, H-2' and H-6'), 12.56 (br s, 1H, N-H). ^1H NMR (d_6-DMSO): δ 6.94 (d, 1H, H-4), 7.34 (d, 1H, H-5), 7.49 (t, 1H, H-4'), 7.52 (d, 2H, H-2' and H-6'), 7.57 (t, 2H, H-3' and H-5'), 13.21 (br s, 1H, N-H). ^{13}C NMR ($CDCl_3$): δ 129.05 (C-4'), 129.59 (C-3' and C-5'), 130.17 (C-1'), 130.19 (C-4), 133.58 (C-2' and C-6'), 134.39 (C-5), 146.71 (C-6), 161.14 (C-3). ^{13}C NMR (d_6-DMSO): δ 128.83 (C-4'), 129.86 (C-3' and C-5'), 130.79 (C-1'), 130.82 (C-4), 132.71 (C-2' and C-6'), 134.65 (C-5), 143.21 (C-6), 159.67 (C-3).

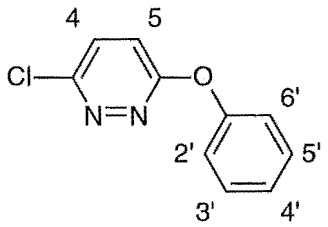


444

3-Chloro-6-phenoxypyridazine, 446.

446 was prepared by the reaction of one equivalent of sodium phenoxide with **442** in benzene as previously reported.[231] NMR analysis of the product showed it to be contaminated by the corresponding bis-ether, **419**, with the product being approximately 85% **446**. Mp 62-63°C (lit.[231] 69-70°C). Calcd for $C_{10}H_7N_2O^{35}Cl$: M^+, 206.0247; Found (EI): M^+, 206.0250. IR (KBr pellet): ν_{max} 1574, 1492, 1409, 1324, 1284, 1258, 1193, 1136, 874, 854, 766 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.14 (d, 1H, H-5), 7.18 (d, 2H, H-2' and H-6'), 7.24 (t, 1H, H-4'), 7.41 (t, 2H, H-3' and H-5'), 7.46 (d, 1H, H-4). ^1H NMR (d_6-DMSO): δ 7.35 (d, 2H, H-2' and H-6'), 7.38 (t, 1H, H-4'), 7.56 (t, 2H, H-3' and H-5'), 7.67 (d, 1H, H-5), 8.04 (d, 1H, H-4). ^{13}C NMR ($CDCl_3$): δ

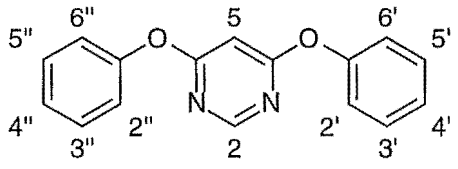
119.93 (C-5), 120.89 (C-2' and C-6'), 125.57 (C-4'), 129.79 (C-3' and C-5'), 131.41 (C-4), 151.94 (C-1'), 165.03 (C-6). ^{13}C NMR (d_6-DMSO): δ 121.15 (C-2' and C-6'), 121.37 (C-5), 125.57 (C-4'), 130.02 (C-3' and C-5'), 132.57 (C-4), 151.86 (C-1'), 165.33 (C-6).



446

4,6-Diphenoxypyrimidine, 420.

A mixture of phenol (2.88 g, 3.1 mmol), potassium carbonate (2.81 g, 2.0 mmol) and 4,6-dichloropyrimidine, **443**, (1.53 g, 1.0 mmol) was heated at 160°C for one hour after which it was allowed to cool to room temperature. Water (10 cm^3) and aqueous potassium hydroxide (0.13 mol dm^{-3}, 30 cm^3) were added and the suspension ultrasonicated to break up the solid. The mixture was filtered and the solid washed with water (50 cm^3) then dried under reduced pressure to give **420** in 89% yield. Mp 109-109.5°C. Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60; Found: C, 72.55; H, 4.42; N, 10.61%. Calcd for $C_{16}H_{12}N_2O_2$: M^+, 264.0899; Found (EI): M^+, 264.0897. IR (KBr pellet): ν_{max} 1606, 1579, 1562, 1489, 1456, 1382, 1240, 1219, 1207, 1152, 820, 763, 695 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.29 (s, 1H, H-5), 7.16 (d, 4H, H-2', H-6', H-2" and H-6"), 7.28 (t, 2H, H-4' and H-4"), 7.44 (t, 4H, H-3', H-5', H-3" and H-5"), 8.45 (s, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 92.11 (C-5), 121.48 (C-2', C-6', C-2" and C-6'), 125.90 (C-4' and C-4"), 129.87 (C-3', C-5', C-3" and C-5"), 152.43 (C-1' and C-1"), 158.42 (C-2), 171.61 (C-4 and C-6).



420

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

420 was reacted with one equivalent of lithium tetrachloropalladate to give Pd(**420**)$_2$Cl$_2$, **452**, in 82% yield. Recrystallisation from nitromethane/toluene gave the analytical sample. Mp 209.5-212°C (dec.). Anal. Calcd for $C_{32}H_{24}N_4O_4Cl_2Pd.^2/_3Ph\text{-}CH_3$: C, 57.40; H, 3.85; N, 7.30; Cl, 9.24; Found: C, 57.24; H, 3.71; N, 7.34; Cl, 9.38%. IR (KBr pellet): ν_{max} 1621, 1582, 1547, 1492, 1469, 1412, 1252, 1204, 749, 685 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.02 (s, 1H, H-5), 7.03 (d, 2H, H-2" and H-6"), 7.27 (t, 1H, H-4"), 7.35 (t, 1H, H-4'), 7.36 (d, 2H, H-2' and H-6'), 7.40 (t, 2H, H-3" and H-5"), 7.46 (t, 2H, H-3' and H-5'), 8.84 (s, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 92.57 (C-5), 121.19 (C-2" and C-6"), 121.29 (C-2' and C-6'), 126.34 (C-4"), 127.14 (C-4'), 129.76 (C-3" and C-5"), 130.49 (C-3' and C-5'), 151.63 (C-1' or C-1"), 152.11 (C-1' or C-1"), 160.30 (C-2), 170.72 (C-4 or C-6), 171.72 (C-4 or C-6).

(ii) REACTION WITH PALLADIUM ACETATE

420 and one equivalent of palladium acetate were reacted according to method B to give [Pd(**420**-H)Cl]$_2$ in 37% yield. Mp 244-245°C (dec.). Anal. Calcd for $C_{32}H_{22}N_4O_4Cl_2Pd_2$: C, 47.34; H, 2.74; N, 6.91; Cl, 8.75; Found: C, 47.44; H, 2.80; N, 6.97; Cl, 8.16%. IR (KBr pellet): ν_{max} 1611, 1585, 1572, 1547, 1491, 1468, 1454, 1431, 1408, 1244, 1198, 758 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.62 (s, 1H, H-5), 6.92 (d, 1H, H-6'), 6.95 (t, 1H, H-4'), 7.08 (t, 1H, H-5'), 7.14 (d, 2H, H-2" and H-6"), 7.34 (t, 1H, H-4"), 7.41 (d, 1H, H-3'), 7.47 (t, 2H, H-3" and H-5"), 8.93 (s, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 94.62 (C-5), 116.48 (C-6'), 121.32 (C-2" and C-6"), 124.85 (C-4'), 126.30 (C-4"), 126.63 (C-5'), 130.10 (C-3" and C-5"), 136.80 (C-3"), 160.00 (C-2).

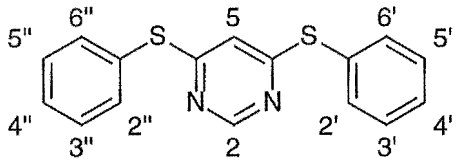
During the preparation of [Pd(**420**-H)Cl]$_2$, a sample of the corresponding μ-diacetato dipalladium complex, [Pd(**420**-H)OAc]$_2$, was isolated and characterised by NMR. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 3H, CH_3COO), 6.23 (s, 1H, H-5), 6.71 (d, 1H, H-6'), 6.84 (t, 1H, H-4'), 6.97 (d, 1H, H-3'), 7.02 (t, 1H, H-5'), 7.04 (d, 2H, H-2" and H-6"), 7.32 (t, 1H, H-4"), 7.47 (t, 2H, H-3" and H-5"), 8.38 (s, 1H, H-2).

Ligand exchange of [Pd(**420**-H)Cl]$_2$ with thallium acetylacetonate gave Pd(**420**-H)(acac), **454**, in 62% yield. Mp 202-206°C (dec.). Anal. Calcd for $C_{21}H_{18}N_2O_4Pd$: C, 53.80; H, 3.87; N, 5.98; Found: C, 53.81; H, 4.16; N, 5.88%. IR (KBr pellet): ν_{max} 1611, 1585, 1548, 1509, 1490. 1471, 1456, 1432, 1394, 1309, 1241, 1227, 1196, 749 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H, acac-CH_3), 2.09 (s, 3H, acac-CH_3), 5.42 (s, 1H, acac-CH), 6.57 (s, 1H, H-5), 6.94 (d, 1H, H-6'), 7.10 (br t, 2H, H-4' and H-5'), 7.17 (d, 2H, H-2" and H-6"), 7.34 (t, 1H, H-4"), 7.49 (t, 2H, H-3" and H-5"), 7.65 (d, 1H, H-3'), 9.19 (s, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 27.56 and 27.71 (acac-CH_3), 93.97 (C-5), 100.44 (acac-CH), 115.53 (C-6'), 119.12 (C-2'), 121.39 (C-2" and C-6"), 124.27 (C-4'), 125.86 (C-4"), 126.52 (C-5'), 130.12 (C-3" and C-5"), 133.70 (C-3'), 145.05 (C-1'), 152.08 (C-1"), 158.91 (C-2), 187.00 and 188.13 (acac-CO).

4,6-Bis(phenylthio)pyrimidine, 424.

Thiophenol (2.1 cm^3, 2.0 mmol) was added to a freshly prepared solution of sodium ethoxide (0.52 g sodium, 2.3 mmol) in ethanol (20 cm^3) and to the resultant solution was added **443** (1.5 g, 1.0 mmol) dissolved in ethanol (20 cm^3). The reaction mixture was stirred under reflux for one day after which it was allowed to cool to room temperature and the precipitate of sodium chloride removed by filtration. The filtrate was chilled and the precipitate filtered to give **424**. The filtrate was stripped of solvent and the residue taken up in water (50 cm^3). Aqueous sodium hydroxide (8 mol dm^{-3}, 5 cm^3) was added and the solution extracted with chloroform (3 x 25 cm^3). The organic extracts were combined, dried over magnesium sulfate and the solvent removed under reduced pressure to give a residue which crystallised upon standing overnight. The supernatant was removed and the solid recrystallised from ethanol to give an additional quantity of the ligand. Total yield 47%. Mp 116.5-117°C. Anal. Calcd for $C_{16}H_{12}N_2S_2$: C, 64.83; H, 4.08; N, 9.45; Found: C, 64.53; H, 3.91; N, 9.44%. Calcd for $C_{16}H_{12}N_2S_2$: M^+, 296.0442; Found (EI): M^+, 296.0443. IR (KBr pellet): ν_{max} 1530, 1494, 1474, 1427, 1281, 1082, 802, 748, 689 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.03 (s, 1H, H-5), 7.31 (t, 4H, H-3', H-5', H-3" and H-5"), 7.36 (t, 2H, H-4' and H-4"), 7.41 (d, 4H, H-2', H-6', H-2" and H-6"), 8.62 (s, 1H, H-2). ^{1}H NMR (d_6-DMSO): δ 6.09 (s, 1H,

H-5), 7.48 (t, 4H, H-3', H-5', H-3" and H-5"), 7.53 (d, 4H, H-2', H-6', H-2" and H-6"), 7.56 (t, 2H, H-4' and H-4"), 8.75 (s, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 111.91 (C-5), 127.28 (C-1' and C-1"), 129.76 (C-3', C-5', C-3" and C-5"), 129.97 (C-4' and C-4"), 135.50 (C-2', C-6', C-2" and C-6'), 156.70 (C-2), 172.20 (C-4 and C-6). ^{13}C NMR (d_6-DMSO): δ 111.10 (C-5), 126.36 (C-1' and C-1"), 130.27 (C-3', C-5', C-3" and C-5"), 130.51 (C-4' and C-4"), 135.33 (C-2', C-6', C-2" and C-6'), 156.78 (C-2), 171.67 (C-4 and C-6).



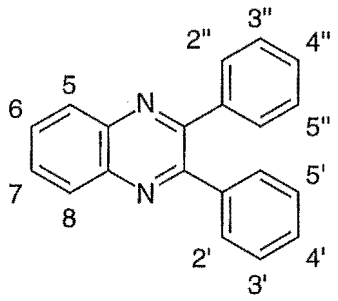
424

(i) REACTION WITH LITHIUM TETRACHLOROPALLADATE

Lithium tetrachloropalladate was reacted with two equivalents of **424** without stirring to give Pd(**424**)$_2$Cl$_2$, **453**, in 93% yield. Mp 241°C (dec.). Anal. Calcd for $C_{32}H_{24}N_4S_4Cl_2Pd$: C, 49.91; H, 3.14; N, 7.28; Cl, 9.21; Found: C, 49.74; H, 3.06; N, 7.42; Cl, 9.34%. IR (KBr pellet): ν_{max} 1547, 1495, 1474, 1429, 1315, 1290, 1157, 822, 745, 687 cm^{-1}. ^{1}H NMR ($CDCl_3$, 23°C): δ 5.79 (br d, 1H, H-5), 7.24-7.50 (br m, 10H, H-2', H-3', H-4', H-5', H-6', H-2", H-3", H-4", H-5" and H-6"), 8.99 (br d, 1H, H-2). ^{1}H NMR ($CDCl_3$, 53°C): δ 5.87 (br s, 1H, H-5), 7.23-7.39 (m, 8H, H-3', H-4', H-5', H-3", H-4", H-5" and H-2' and H-6' or H-2" and H-6"), 7.48 (d, 2H, H-2' and H-6' or H-2" and H-6"), 8.97 (br s, 1H, H-2). ^{13}C NMR ($CDCl_3$, 23°C): δ 113.73 and 113.91 (C-5), 126.22 (C-1' and C-1"), 130.07 (C-3' and C-5' or C-3" and C-5"), 130.27 (C-3' and C-5' or C-3" and C-5"), 130.52 (C-4' or C-4"), 130.85 (C-4' or C-4"), 135.42 (C-2' and C-6' or C-2" and C-6"), 135.79 (C-2' and C-6' or C-2" and C-6"), 157.26 and 157.62 (C-2). ^{13}C NMR ($CDCl_3$, 53°C): δ 114.09 (C-5), 127.26 (C-1' and C-1"), 130.07 (C-3' and C-5' or C-3" and C-5"), 130.29 (C-3' and C-5' or C-3" and C-5"), 130.47 (C-4' or C-4"), 130.84 (C-4' or C-4"), 135.46 (C-2' and C-6' or C-2" and C-6"), 135.85 (C-2' and C-6' or C-2" and C-6"), 157.73 (C-2).

2,3-Diphenylquinoxaline, 458.

458 was available in the department. ^{1}H NMR ($CDCl_3$): δ 7.35 (m, 6H, H-3', H-4', H-5', H-3", H-4" and H-5"), 7.53 (m, 4H, H-2', H-6', H-2" and H-6"), 7.79 (m, 2H, H-6 and H-7), 8.19 (m, H-5 and H-8).



458

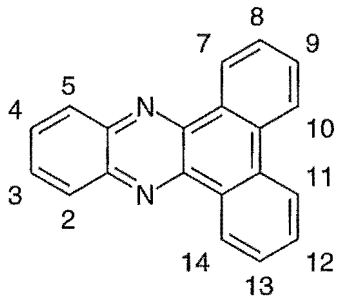
(i) REACTION WITH RHODIUM TRICHLORIDE

Reaction of **458** with rhodium trichloride trihydrate gave [Rh(**458**-H)$_2$Cl]$_2$ in 62% yield. ^{1}H NMR ($CDCl_3$): δ 5.73 (d, 1H, H-3'), 6.26 (t, 1H, H-4'), 6.50 (t, 1H, H-5'), 6.70 (t, 1H, H-7), 6.90 (d, 1H, H-6'), 7.27 (t, 1H, H-6), 7.65 (d, 1H, H-5), 7.67 (br m, 3H, H-3", H-4" and H-5"), 8.12 (br d, 2H, H-2" and H-6"), 8.74 (d, 1H, H-8).

Ligand exchange of [Rh(**458**-H)$_2$Cl]$_2$ with sodium acetylacetonate gave Rh(**458**-H)$_2$(acac), **460**, in 74% yield. Mp >300°C. Calcd for $C_{45}H_{33}N_4O_2Rh$: M^+, 764.1659; Found(FAB): M^+, 764.1648. ^{1}H NMR ($CDCl_3$): δ 1.62 (s, 6H, acac-CH_3), 4.65 (s, 1H, acac-CH), 6.52 (d, 2H, H-3'), 6.60 (t, 2H, H-4'), 6.67 (t, 2H, H-5'), 7.08 (d, 2H, H-6'), 7.55 (t, 2H, H-7), 7.61 (br m, 6H, H-3", H-4" and H-5"), 7.69 (t, 2H, H-6), 8.00 (br d, 4H, H-2" and H-6"), 8.12 (d, 2H, H-5), 8.48 (d, 2H, H-8). ^{13}C NMR ($CDCl_3$): complex not sufficiently soluble to obtain data.

Dibenzo[a,c]phenazine, 459.

459 was available in the department. ^{1}H NMR ($CDCl_3$): δ 7.75 (t, 2H, H-8 and H-13), 7.81 (t, 2H, H-9 and H-12), 7.86 (m, 2H, H-3 and H-4), 8.34 (m, 2H, H-2 and H-5), 8.58 (d, 2H, H-10 and H-11), 9.42 (d, 2H, H-7 and H-14).



459

(i) REACTION WITH RHODIUM TRICHLORIDE

Reaction of **459** with rhodium trichloride trihydrate gave [Rh(**459**-H)$_2$Cl]$_2$ in quantitative yield. ^{1}H NMR ($CDCl_3$): δ 6.14 (br d, 1H, H-13), 6.94 (br t, 1H, H-12), 7.78 (m, 1H, H-8), 7.81 (m, 1H, H-9), 7.92 (d, 1H, H-11), 7.96 (br m, 2H, H-3 and H-4), 8.43 (m, 1H, H-10), 8.49 (br m, 1H, H-5), 9.44 (m, 1H, H-7), 10.11 (br s, 1H, H-2).

Ligand exchange of [Rh(**459**-H)$_2$Cl]$_2$ with sodium acetylacetonate gave Rh(**459**-H)$_2$(acac), **461**, in 82% yield. Mp > 300°C. Calcd for $C_{45}H_{30}N_4O_2Rh$: *MH*$^+$, 761.1424; Found(FAB): *MH*$^+$, 761.1414. ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 6H, acac-CH_3), 4.91 (s, 1H, acac-CH), 6.49 (d, 2H, H-13), 7.03 (t, 2H, H-12), 7.71 (t, 2H, H-3), 7.78 (m, 2H, H-8), 7.83 (m, 2H, H-9), 7.88 (t, 2H, H-4), 8.01 (d, 2H, H-11), 8.46 (d, 2H, H-5), 8.51 (d, 2H, H-10), 8.89 (d, 2H, H-2), 9.45 (d, 2H, H-7). ^{13}C NMR ($CDCl_3$): complex not sufficiently soluble to obtain data.

Crystallography

X-RAY CRYSTALLOGRAPHY

Intensity data were collected with a Nicolet R3m four-circle diffractometer, or in the case of **455**, with a SMART CCD area detector, using graphite-monochromatised Mo Kα radiation (λ 0.7107 Å). Cell parameters were determined by least-squares refinement using the setting angles of accurately centred reflections with $2\theta > 20°$. Throughout data collections (ω scans) the intensities of three standard reflections were monitored and, in most cases, this showed no significant crystal decomposition. However, crystals of **304** were obtained as very fine plates that rapidly decomposed at room temperature. The plates were also prone to cracking at low temperature. Several attempts were made to collect full data sets from these crystals, but in no case was this successful. The data used were obtained from an incomplete shell of low angle ($2\theta_{max}$ 36°) reflections obtained prior to the sudden decomposition of the crystal. The intensities of all data sets were corrected for Lorentz and polarisation effects and for absorption by a procedure based on azimuthal ψ scans.

All structures were solved by direct methods using SHELXS-90[285] and refined on F^2 by full-matrix least squares procedures using SHELXL-93.[286] In general, all non-hydrogen atoms were refined with anisotropic displacement parameters. However, due to the paucity of data for structure of **304** only the rhodium and chlorine atoms were made anisotropic. Hydrogens were included in calculated positions and were assigned isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. All data were used in the refinements; the functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$ where $P = [\max(F_0^2) + 2F_c^2]/3$. The site occupancies of the disordered solvate molecules were determined by refinement.

Final atomic coordinates and equivalent isotropic displacement parameters (defined as one third of the trace of the orthogonalised U_{ij} tensor) are listed in Tables 2-6. Final bonding geometries are listed in Tables 7-10.

Table 1 X-ray crystal data and details of data collections and structure refinements

Compound	**234**	**455**	**302**	**304**	**309**
Formula	$C_{22}H_{18}Cl_2N_2O_2Pd$	$C_{21}H_{18}N_2O_4Pd$	$C_{24}H_{18}Cl_3N_2O_6Rh$	$C_{28}H_{24}Cl_3N_4O_6Rh$	$C_{16}H_{20}Cl_2NO_3S_2Rh$[a]
Formula Weight	519.7	468.8	639.7	721.8	611.0
Crystal System	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
a (Å)	9.385(3)	13.0994(3)	19.705(4)	27.36(2)	16.399(2)
b (Å)	8.516(3)	14.4413(4)	7.839(1)	9.960(9)	7.916(1)
c (Å)	13.171(4)	20.1011(4)	15.748(3)	22.10(1)	19.012(3)
β (°)	101.88(2)	90	97.25(1)	93.75(2)	103.32(1)
V (Å^3)	1030.1(6)	3802.6(2)	2413(1)	6010(7)	2401(1)
Space Group	$P2_1/c$	$P2_12_12_1$	C2/c	C2/c	$P2_1/n$
Z	2	8	4	8	4
D_c (Mg m^{-3})	1.68	1.64	1.76	1.60	1.69
F(000)	520	1888	1280	2912	1232
Temperature (K)	132(2)	142(2)	130(2)	130(2)	130(2)
Crystal Size (mm)	0.45 x 0.21 x 0.11	0.53 x 0.35 x 0.13	0.44 x 0.21 x 0.18	0.42 x 0.35 x 0.01	0.62 x 0.30 x 0.06
μ (mm^{-1})	1.18	1.48	1.09	0.88	1.34
$2\theta_{max}$(°)	48	53	55	36	47
Unique reflections	1625	7048	2776	1336	3513
Parameters	133	509	165	204	283
GooF	1.07	1.07	1.04	1.07	1.04
R[b] [I > 2σ(I)]	0.040	0.022	0.031	0.049	0.041
wR[c] (all data)	0.099	0.050	0.069	0.080	0.102

[a] Also includes 0.5DMSO and 0.5$CHCl_3$ disordered solvate. [b] $R = \Sigma (|F_o| - |F_c|)/\Sigma |F_o|$. [c] $wR = (\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$.

Table 2 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **234**.

Atom	10^4 x	10^4 y	10^4 z	10^3 U_{eq}
Pd1	0	0	5000	19(1)
Cl1	-1199(2)	967(2)	6211(1)	29(1)
N1	866(5)	2147(5)	4838(3)	19(1)
C2	2008(6)	2713(7)	5514(4)	22(1)
C3	2583(6)	4166(7)	5408(5)	25(1)
C4	1933(6)	5089(8)	4579(4)	26(1)
C5	771(6)	4500(7)	3870(5)	25(1)
C6	273(6)	3030(7)	4025(4)	22(1)
O1	2554(4)	1684(5)	6283(3)	32(1)
C1'	3702(7)	2210(7)	7077(4)	23(2)
C2'	5116(7)	2060(8)	6948(5)	37(2)
C3'	6214(8)	2511(9)	7739(6)	48(2)
C4'	5936(8)	3099(8)	8640(6)	45(2)
C5'	4534(10)	3244(9)	8751(5)	47(2)
C6'	3389(8)	2830(8)	7946(5)	38(2)

Table 3 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **455**.

Atom	10^4 x	10^4 y	10^4 z	10^3 U_{eq}
Pd1	1191(1)	-1476(1)	3415(1)	16(1)
N1	3016(2)	-650(2)	2889(1)	18(1)
N2	2663(2)	-1483(2)	3129(1)	18(1)
C3	3293(2)	-2193(2)	3196(1)	20(1)
C4	4346(2)	-2121(2)	3043(2)	25(1)
C5	4702(2)	-1303(2)	2812(1)	28(1)
C6	3978(2)	-575(2)	2750(1)	21(1)
O3	2981(1)	-3022(1)	3429(1)	24(1)
C1'	2001(2)	-3367(2)	3246(1)	20(1)
C2'	1151(2)	-2803(2)	3188(1)	19(1)
C3'	263(2)	-3232(2)	2952(1)	21(1)
C4'	222(3)	-4173(2)	2804(1)	25(1)
C5'	1087(3)	-4719(2)	2910(1)	28(1)
C6'	1986(2)	-4317(2)	3124(1)	24(1)
O6	4354(2)	252(1)	2538(1)	27(1)
C1"	3677(2)	1012(2)	2491(1)	20(1)
C2"	2973(2)	1057(2)	1982(1)	23(1)
C3"	2389(2)	1845(2)	1924(2)	27(1)
C4"	2484(2)	2567(2)	2377(1)	25(1)
C5"	3189(2)	2503(2)	2889(1)	24(1)
C6"	3809(2)	1726(2)	2948(1)	23(1)
O1	1277(2)	-73(1)	3644(1)	21(1)
O2	-293(1)	-1535(1)	3707(1)	22(1)
C11	752(2)	1421(2)	3951(1)	27(1)
C12	541(2)	409(2)	3858(1)	19(1)
C13	-448(2)	66(2)	4014(1)	19(1)

C14	-791(2)	-837(2)	3947(1)	19(1)
C15	-1866(2)	-1064(2)	4168(2)	25(1)
Pd1A	14066(1)	-1327(1)	900(1)	15(1)
N1A	13318(2)	376(2)	374(1)	17(1)
N2A	14207(2)	-9(2)	597(1)	16(1)
C3A	15048(2)	494(2)	646(1)	18(1)
C4A	15051(2)	1458(2)	509(1)	21(1)
C5A	14169(2)	1844(2)	297(1)	22(1)
C6A	13315(2)	1264(2)	234(1)	18(1)
O3A	15944(1)	118(1)	837(1)	23(1)
C1'A	16206(2)	-802(2)	651(1)	18(1)
C2'A	15498(2)	-1515(2)	623(1)	17(1)
C3'A	15866(2)	-2373(2)	396(1)	20(1)
C4'A	16888(2)	-2505(2)	235(1)	24(1)
C5'A	17580(2)	-1778(2)	303(1)	24(1)
C6'A	17240(2)	-916(2)	513(1)	23(1)
O6A	12430(2)	1667(1)	27(1)	21(1)
C1"A	11541(2)	1107(2)	-24(1)	18(1)
C2"A	11494(2)	394(2)	-485(1)	20(1)
C3"A	10590(2)	-99(2)	-537(1)	22(1)
C4"A	9755(2)	108(2)	-131(1)	24(1)
C5"A	9826(2)	833(2)	324(1)	25(1)
C6"A	10717(2)	1339(2)	377(1)	20(1)
O1A	12574(2)	-1074(1)	1197(1)	20(1)
O2A	13983(2)	-2661(1)	1191(1)	20(1)
C11A	10902(2)	-1361(2)	1563(2)	29(1)
C12A	11975(2)	-1685(2)	1424(1)	19(1)
C13A	12230(2)	-2618(2)	1549(1)	19(1)
C14A	13171(2)	-3034(2)	1439(1)	19(1)
C15A	13300(2)	-4043(2)	1629(2)	26(1)

Table 4 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **302**.

Atom	10^4 x	10^4 y	10^4 z	10^3 U_{eq}
Rh	2500	2500	0	9.25(8)
Cl	2347.7(3)	5428.0(8)	88.4(4)	15.0(1)
N(1)	2420(1)	2360(3)	1264(1)	13(1)
C(2)	1759(1)	2417(4)	1441(2)	14(1)
C(3)	1609(1)	2709(4)	2268(2)	18(1)
C(4)	2152(2)	2834(4)	2928(2)	22(1)
C(5)	2817(2)	2654(4)	2744(2)	22(1)
C(6)	2937(1)	2447(4)	1894(2)	16(1)
C(1)	1255(1)	2237(3)	665(2)	13(1)
O(1)	1481(1)	2253(2)	-49(1)	13(1)
C(1')	518(1)	2053(3)	681(2)	16(1)
C(2')	78(1)	2823(4)	25(2)	20(1)
C(3')	-626(1)	2625(5)	15(2)	28(1)
C(4')	-875(2)	1607(5)	624(2)	32(1)
C(5')	-441(2)	791(4)	1248(2)	29(1)
C(6')	262(2)	1024(4)	1297(2)	22(1)
Cl(1)	0	6107(1)	2500	25.5(6)
O(11)	-356(2)	5094(5)	1842(2)	84(1)
O(12)	-484(1)	7164(4)	2857(2)	58(1)

Table 5 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **304**.

Atom	10^4 x	10^4 y	10^4 z	10^3 U_{eq}
Rh(1)	2856.1(5)	249.7(9)	1409.9(4)	17.4(5)
Cl(1)	2235(2)	1539(3)	1743(1)	25(2)
Cl(2)	2423(2)	-1700(3)	1552(1)	23(2)
N(1)	2602(4)	222(9)	536(3)	16(3)
C(2)	2866(5)	-547(10)	175(4)	7(3)
C(3)	2748(5)	-645(10)	-442(5)	24(4)
C(4)	2327(5)	44(10)	-684(4)	18(3)
C(5)	2076(5)	833(10)	-311(5)	24(4)
C(6)	2228(5)	895(10)	298(4)	10(4)
C(1)	3313(5)	-1160(10)	488(4)	8(3)
O(1)	3391(3)	-863(6)	1037(3)	14(2)
C(1')	3664(6)	-1932(11)	182(5)	18(4)
C(2')	3528(6)	-2971(11)	-218(5)	24(4)
C(3')	3907(6)	-3719(11)	-491(5)	29(4)
C(4')	4383(6)	-3439(11)	-330(5)	33(4)
C(5')	4522(6)	-2397(11)	78(5)	30(4)
C(6')	4156(6)	-1647(10)	319(4)	4(3)
N(1A)	3168(4)	386(8)	2258(3)	14(3)
C(2A)	3430(5)	1569(10)	2358(4)	8(3)
C(3A)	3655(5)	1818(11)	2913(4)	19(4)
C(4A)	3663(5)	873(10)	3375(5)	14(4)
C(5A)	3401(5)	-299(11)	3273(4)	15(3)
C(6A)	3159(5)	-532(10)	2704(4)	11(3)
C(1A)	3427(5)	2398(10)	1829(5)	17(4)
O(1A)	3257(3)	1974(7)	1332(3)	15(2)
C(1'A)	3631(5)	3787(10)	1831(4)	10(3)
C(2'A)	3492(5)	4718(10)	2250(4)	13(3)
C(3'A)	3669(5)	6048(11)	2186(5)	21(4)
C(4'A)	3929(5)	6402(12)	1709(5)	29(4)
C(5'A)	4093(5)	5470(11)	1306(5)	30(4)
C(6'A)	3920(5)	4153(11)	1358(5)	24(4)
Cl(11)	4017(2)	-8102(3)	-229(1)	44(2)
O(11)	4306(4)	-8961(8)	-576(4)	43(3)
O(12)[a]	4200(7)	-8398(14)	408(6)	51(5)
O(13)[a]	3507(8)	-8571(15)	-272(7)	53(6)
O(14)[a]	4081(8)	-6833(17)	-351(8)	66(6)
O(12A)[b]	3708(13)	-8536(22)	166(11)	57(8)
O(13A)[b]	3745(10)	-7272(20)	-724(10)	54(8)
O(14A)[b]	4351(9)	-7010(18)	60(8)	29(7)
N(11)	4366(5)	-257(11)	2085(4)	53(4)
C(11)	4621(6)	356(12)	1816(5)	32(4)
C(12)	4957(6)	1085(15)	1460(6)	85(6)
N(21)	4568(5)	-4377(11)	-1814(5)	56(4)
C(21)	4612(6)	-5504(14)	-1780(6)	52(5)
C(22)	4670(6)	-6962(12)	-1732(6)	62(5)

[a] Disordered; site occupancy 0.6. [b] Disordered; site occupancy 0.4.

Table 6 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **309**.

Atom	10^4 x	10^4 y	10^4 z	10^3 U_{eq}
Rh(1)	2872.9(3)	1623.0(5)	-41.0(2)	12.5(2)
Cl(1)	3681.5(9)	-721(2)	467.8(7)	21.0(3)
Cl(2)	2605.9(9)	2390(2)	1076.7(7)	21.6(3)
N(1)	3184(3)	1078(5)	-1001(2)	15(1)
C(2)	2644(4)	793(7)	-1636(3)	20(1)
C(3)	2915(4)	540(8)	-2260(3)	27(1)
C(4)	3748(4)	616(8)	-2247(3)	30(2)
C(5)	4306(3)	891(7)	-1593(3)	19(1)
C(6)	4012(3)	1124(7)	-985(3)	19(1)
C(7)	1725(4)	574(7)	-1675(3)	20(1)
O(7)	1244(3)	727(6)	-2269(2)	30(1)
C(1')	1422(3)	-48(7)	-1053(3)	18(1)
C(2')	1856(3)	151(6)	-333(3)	14(1)
C(3')	1527(3)	-605(7)	203(3)	19(1)
C(4')	797(4)	-1515(7)	38(3)	24(1)
C(5')	355(4)	-1690(7)	-674(3)	27(1)
C(6')	672(4)	-963(7)	-1211(3)	25(1)
S(1)	4542.7(9)	3180(2)	1035.3(7)	18.4(3)
O(1)	4004(2)	3276(4)	264(2)	16(1)
C(11)	5574(3)	3528(8)	926(3)	24(1)
C(12)	4404(4)	5157(7)	1435(3)	27(1)
S(2)	2095.1(9)	3831(2)	-513.1(7)	15.8(3)
O(2)	1940(3)	3985(5)	-1303(2)	30(1)
C(21)	1105(3)	3889(8)	-282(3)	26(1)
C(22)	2545(4)	5741(7)	-118(3)	27(2)
C(1S)[a]	3813(7)	785(15)	2669(7)	19(3)
Cl(3)[a]	4699(2)	1963(6)	2901(2)	51(1)
Cl(4)[a]	4020(3)	-1365(5)	2744(3)	61(1)
Cl(5)[a]	3007(3)	1396(6)	3071(2)	55(1)
S(3)[a]	3667(7)	823(7)	3142(4)	149(4)
O(3)[a]	4247(8)	353(14)	3830(6)	67(3)
C(31)[a]	4039(19)	2406(38)	2865(15)	134(10)
C(32)[a]	3657(15)	-748(32)	2512(13)	93(8)

[a] Site occupancy 0.5.

Table 7 Bond lengths (Å) and angles (degrees) for **234**.

Pd1-N1	2.029(5)	Pd1-Cl1	2.286(2)	N1-C6	1.332(7)
N1-C2	1.335(7)	C2-O1	1.358(7)	C2-C3	1.368(8)
C3-C4	1.382(8)	C4-C5	1.375(8)	C5-C6	1.366(8)
O1-C1'	1.410(7)	C1'-C6'	1.347(9)	C1'-C2'	1.378(8)
C2'-C3'	1.361(9)	C3'-C4'	1.362(10)	C4'-C5'	1.359(10)
C5'-C6'	1.391(9)				

N1-Pd1-Cl1	90.82(13)	N1A-Pd1-Cl1	89.19(13
Cl1-Pd1-Cl1A	180.0		
C6-N1-C2	118.5(5)	C6-N1-Pd1	118.9(4)
C2-N1-Pd1	122.6(4)	N1-C2-O1	113.1(5)
N1-C2-C3	122.6(5)	O1-C2-C3	124.3(5)
C2-C3-C4	118.4(6)	C5-C4-C3	119.2(6)
C6-C5-C4	118.7(6)	N1-C6-C5	122.6(5)
C2-O1-C1'	117.5(5)	C6'-C1'-C2'	121.7(6)
C6'-C1'-O1	119.2(6)	C2'-C1'-O1	119.2(5)
C3'-C2'-C1'	118.4(6)	C2'-C3'-C4'	121.3(7)
C5'-C4'-C3'	119.4(6)	C4'-C5'-C6'	120.5(7)
C1'-C6'-C5'	118.6(7)		

Table 8. Bond lengths (Å) and angles (degrees) for **455**.

Pd1-C2'	1.972(3)	Pd1-N2	2.012(2)	Pd1-O2	2.032(2)
Pd1-O1	2.080(2)	N1-C6	1.297(4)	N1-N2	1.376(3)
N2-C3	1.322(4)	C3-O3	1.349(3)	C3-C4	1.417(4)
C4-C5	1.353(4)	C5-C6	1.421(4)	C6-O6	1.360(3)
O3-C1'	1.426(3)	C1'-C2'	1.384(4)	C1'-C6'	1.394(4)
C2'-C3'	1.401(4)	C3'-C4'	1.392(4)	C4'-C5'	1.397(4)
C5'-C6'	1.382(4)	O6-C1"	1.414(3)	C1"-C2"	1.378(4)
C1"-C6"	1.391(4)	C2"-C3"	1.376(4)	C3"-C4"	1.390(4)
C4"-C5"	1.387(4)	C5"-C6"	1.390(4)	O1-C12	1.264(3)
O2-C14	1.294(3)	C11-C12	1.498(4)	C12-C13	1.423(4)
C13-C14	1.386(4)	C14-C15	1.512(4)	Pd1A-C2'A	1.974(3)
Pd1A-N2A	2.006(2)	Pd1A-O2A	2.018(2)	Pd1A-O1A	2.076(2)
N1A-C6A	1.313(3)	N1A-N2A	1.365(3)	N2A-C3A	1.323(4)
C3A-O3A	1.351(3)	C3A-C4A	1.418(4)	C4A-C5A	1.352(4)
C5A-C6A	1.404(4)	C6A-O6A	1.362(3)	O3A-C1'A	1.422(3)
C1'A-C2'A	1.387(4)	C1'A-C6'A	1.392(4)	C2'A-C3'A	1.406(4)
C3'A-C4'A	1.391(4)	C4'A-C5'A	1.394(4)	C5'A-C6'A	1.387(4)
O6A-C1"A	1.423(3)	C1"A-C2"A	1.386(4)	C1"A-C6"A	1.388(4)
C2"A-C3"A	1.384(4)	C3"A-C4"A	1.398(4)	C4"A-C5"A	1.394(4)
C5"A-C6"A	1.380(4)	O1A-C12A	1.267(3)	O2A-C14A	1.292(3)
C11A-C12A	1.507(4)	C12A-C13A	1.411(4)	C13A-C14A	1.389(4)
C14A-C15A	1.515(4)				

C2'-Pd1-N2	87.35(11)	C2'-Pd1-O2	90.02(10)
N2-Pd1-O2	177.26(9)	C2'-Pd1-O1	178.32(10)
N2-Pd1-O1	90.97(8)	O2-Pd1-O1	91.66(8)
C6-N1-N2	118.4(2)	C3-N2-N1	120.3(2)
C3-N2-Pd1	125.0(2)	N1-N2-Pd1	114.6(2)
N2-C3-O3	122.3(3)	N2-C3-C4	121.9(3)
O3-C3-C4	115.8(2)	C5-C4-C3	118.3(3)
C4-C5-C6	116.5(3)	N1-C6-O6	119.5(3)
N1-C6-C5	124.6(3)	O6-C6-C5	115.8(2)
C3-O3-C1'	119.5(2)	C2'-C1'-C6'	123.6(3)
C2'-C1'-O3	122.7(2)	C6'-C1'-O3	113.7(3)
C1'-C2'-C3'	115.9(2)	C1'-C2'-Pd1	122.1(2)
C3'-C2'-Pd1	122.0(2)	C4'-C3'-C2'	122.3(3)
C3'-C4'-C5'	119.2(3)	C6'-C5'-C4'	120.1(3)
C5'-C6'-C1'	118.7(3)	C6-O6-C1"	118.4(2)

C2"-C1"-C6"	122.5(3)	C2"-C1"-O6	120.4(2)
C6"-C1"-O6	116.9(2)	C3"-C2"-C1"	118.3(3)
C2"-C3"-C4"	120.9(3)	C5"-C4"-C3"	119.8(3)
C4"-C5"-C6"	120.3(3)	C5"-C6"-C1"	118.1(3)
C12-O1-Pd1	124.8(2)	C14-O2-Pd1	123.8(2)
O1-C12-C13	125.2(3)	O1-C12-C11	116.1(2)
C13-C12-C11	118.7(2)	C14-C13-C12	127.0(3)
O2-C14-C13	127.3(3)	O2-C14-C15	114.3(2)
C13-C14-C15	118.4(2)	C2'A-Pd1A-N2A	87.61(10)
C2'A-Pd1A-O2A	90.09(9)	N2A-Pd1A-O2A	177.70(9)
C2'A-Pd1A-O1A	177.75(10)	N2A-Pd1A-O1A	90.38(8)
O2A-Pd1A-O1A	91.92(7)	C6A-N1A-N2A	118.1(2)
C3A-N2A-N1A	120.7(2)	C3A-N2A-Pd1A	125.1(2)
N1A-N2A-Pd1A	114.0(2)	N2A-C3A-O3A	121.6(2)
N2A-C3A-C4A	121.8(3)	O3A-C3A-C4A	116.6(2)
C5A-C4A-C3A	117.6(3)	C4A-C5A-C6A	117.6(2)
N1A-C6A-O6A	119.1(2)	N1A-C6A-C5A	124.1(2)
O6A-C6A-C5A	116.8(2)	C3A-O3A-C1'A	120.7(2)
C2'A-C1'A-C6'A	123.7(3)	C2'A-C1'A-O3A	122.9(2)
C6'A-C1'A-O3A	113.4(2)	C1'A-C2'A-C3'A	115.9(2)
C1'A-C2'A-Pd1A	121.5(2)	C3'A-C2'A-Pd1A	122.6(2)
C4'A-C3'A-C2'A	121.8(3)	C3'A-C4'A-C5'A	120.0(3)
C6'A-C5'A-C4'A	119.8(3)	C5'A-C6'A-C1'A	118.6(3)
C6A-O6A-C1"A	118.4(2)	C2"A-C1"A-C6"A	122.2(3)
C2"A-C1"A-O6A	120.5(2)	C6"A-C1"A-O6A	117.2(2)
C3"A-C2"A-C1"A	118.0(3)	C2"A-C3"A-C4"A	121.0(3)
C5"A-C4"A-C3"A	119.4(3)	C6"A-C5"A-C4"A	120.3(3)
C5"A-C6"A-C1"A	119.0(2)	C12A-O1A-Pd1A	124.4(2)
C14A-O2A-Pd1A	123.7(2)	O1A-C12A-C13A	125.6(3)
O1A-C12A-C11A	115.4(2)	C13A-C12A-C11A	119.0(2)
C14A-C13A-C12A	126.6(3)	O2A-C14A-C13A	127.7(2)
O2A-C14A-C15A	113.9(2)	C13A-C14A-C15A	118.4(2)

Table 9 Bond lengths (Å) and angles (degrees) for **302** and **304**.

	302	**304**		**304**
Rh(1)-N(1)	2.019(2)	2.009(8)	Rh(1)-N(1A)	2.013(8)
Rh(1)-O(1)	2.009(2)	2.051(8)	Rh(1)-O(1A)	2.051(8)
Rh(1)-Cl(1)	2.3212(7)	2.290(4)	N(1A)-C(6A)	1.35(1)
Rh(1)-Cl(2)		2.307(4)	N(1A)-C(2A)	1.39(1)
N(1)-C(6)	1.332(3)	1.31(1)	C(2A)-C(3A)	1.36(1)
N(1)-C(2)	1.367(3)	1.35(1)	C(2A)-C(1A)	1.43(1)
C(2)-C(3)	1.390(3)	1.38(1)	C(3A)-C(4A)	1.39(1)
C(2)-C(1)	1.481(3)	1.50(2)	C(4A)-C(5A)	1.38(2)
C(3)-C(4)	1.398(4)	1.42(2)	C(5A)-C(6A)	1.40(1)
C(4)-C(5)	1.385(4)	1.36(2)	C(1A)-O(1A)	1.24(1)
C(5)-C(6)	1.398(4)	1.38(1)	C(1A)-C(1'A)	1.49(2)
C(1)-O(1)	1.261(3)	1.25(1)	C(1'A)-C(2'A)	1.38(1)
C(1)-C(1')	1.463(3)	1.43(2)	C(1'A)-C(6'A)	1.40(2)
C(1')-C(6')	1.404(4)	1.39(2)	C(2'A)-C(3'A)	1.42(1)
C(1')-C(2')	1.399(4)	1.40(1)	C(3'A)-C(4'A)	1.36(2)
C(2')-C(3')	1.393(4)	1.44(2)	C(4'A)-C(5'A)	1.38(2)
C(3')-C(4')	1.385(5)	1.36(2)	C(5'A)-C(6'A)	1.40(2)
C(4')-C(5')	1.376(5)	1.41(2)	Cl(11)-O(12A)	1.33(3)
C(5')-C(6')	1.390(4)	1.38(2)	Cl(11)-O(13A)	1.53(2)
Cl(11)-O(11)	1.419(3)	1.42(1)	Cl(11)-O(14A)	1.53(2)
Cl(11)-O(12)	1.431(3)	1.49(2)	N(11)-C(11)	1.13(2)
Cl(11)-O(13)		1.47(2)	C(11)-C(12)	1.44(2)
Cl(11)-O(14)		1.31(2)	N(21)-C(21)	1.13(2)
			C(21)-C(22)	1.46(2)

	302	304		304
N(1)-Rh(1)-N(1A)	180.0	174.2(4)	N(1A)-Rh(1)-O(1A)	79.9(3)
N(1)-Rh(1)-O(1)	80.25(8)	79.5(3)	N(1A)-Rh(1)-Cl(2)	96.9(3)
N(1)-Rh(1)-O(1A)	99.75(8)	94.8(3)	N(1A)-Rh(1)-O(1)	98.1(3)
O(1A)-Rh(1)-O(1)	180.0	91.1(3)	N(1)-Rh(1)-Cl(2)	88.3(3)
N(1)-Rh(1)-Cl(1)	88.17(7)	95.7(3)	O(1)-Rh(1)-Cl(2)	89.2(2)
N(1A)-Rh(1)-Cl(1)	91.83(7)	86.6(3)	O(1A)-Rh(1)-Cl(2)	176.9(2)
O(1)-Rh(1)-Cl(1)	87.79(5)	175.1(2)	C(6A)-N(1A)-C(2A)	119.6(8)
O(1A)-Rh(1)-Cl(1)	92.21(5)	88.3(3)	C(6A)-N(1A)-Rh(1)	127.5(7)
Cl(1)-Rh(1)-Cl(2)	180.0	91.7(1)	C(2A)-N(1A)-Rh(1)	112.8(6)
C(6)-N(1)-C(2)	120.4(2)	119.2(9)	C(3A)-C(2A)-N(1A)	119.8(9)
C(6)-N(1)-Rh(1)	125.7(2)	126.4(8)	C(3A)-C(2A)-C(1A)	127.6(11)
C(2)-N(1)-Rh(1)	113.2(2)	114.3(8)	N(1A)-C(2A)-C(1A)	112.6(9)
N(1)-C(2)-C(3)	121.1(2)	121.7(11)	C(2A)-C(3A)-C(4A)	121.7(11)
N(1)-C(2)-C(1)	112.7(2)	114.3(9)	C(5A)-C(4A)-C(3A)	118.0(10)
C(3)-C(2)-C(1)	126.1(2)	123.8(11)	C(4A)-C(5A)-C(6A)	119.9(10)
C(2)-C(3)-C(4)	118.4(2)	117.9(11)	N(1A)-C(6A)-C(5A)	120.8(10)
C(5)-C(4)-C(3)	119.5(2)	118.8(10)	O(1A)-C(1A)-C(2A)	120.6(10)
C(4)-C(5)-C(6)	119.4(2)	119.1(13)	O(1A)-C(1A)-C(1'A)	116.0(9)
N(1)-C(6)-C(5)	120.9(2)	123.1(11)	C(2A)-C(1A)-C(1'A)	123.4(10)
O(1)-C(1)-C(1')	118.7(2)	120.4(12)	C(1A)-O(1A)-Rh(1)	112.5(7)
O(1)-C(1)-C(2)	117.3(2)	115.7(11)	C(2'A)-C(1'A)-C(6'A)	121.3(10)
C(1')-C(1)-C(2)	124.0(2)	123.7(9)	C(2'A)-C(1'A)-C(1A)	120.3(11)
C(1)-O(1)-Rh(1)	115.5(2)	115.9(8)	C(6'A)-C(1'A)-C(1A)	118.0(10)
C(6')-C(1')-C(2')	121.0(2)	120.2(13)	C(1'A)-C(2'A)-C(3'A)	116.6(11)
C(6')-C(1')-C(1)	120.9(3)	117.2(11)	C(4'A)-C(3'A)-C(2'A)	121.3(11)
C(2')-C(1')-C(1)	118.0(2)	122.5(14)	C(3'A)-C(4'A)-C(5'A)	122.3(11)
C(1')-C(2')-C(3')	118.9(3)	118.7(14)	C(4'A)-C(5'A)-C(6'A)	116.8(12)
C(4')-C(3')-C(2')	119.7(3)	119.2(12)	C(1'A)-C(6'A)-C(5'A)	121.0(11)
C(3')-C(4')-C(5')	121.3(3)	122.2(14)	O(12A)-Cl(11)-O(11)	123.9(11)
C(6')-C(5')-C(4')	120.2(3)	118.0(14)	O(14)-Cl(11)-O(13)	115.7(12)
C(5')-C(6')-C(1')	118.7(3)	121.5(11)	O(12A)-Cl(11)-O(13A)	110(2)
O(11)-Cl(11)-O(12)	108.5(2)	103.1(8)	O(11)-Cl(11)-O(13A)	101.7(9)
O(11)-Cl(11)-O(13)	112.0(4)	109.4(8)	O(12A)-Cl(11)-O(14A)	110.1(14)
O(14)-Cl(11)-O(11)	109.3(2)	112.7(9)	O(11)-Cl(11)-O(14A)	108.5(10)
O(14)-Cl(11)-O(12)	109.3(3)	110.2(10)	O(13A)-Cl(11)-O(14A)	99.5(11)
O(13)-Cl(11)-O(12)	109.2(2)	104.8(9)	N(11)-C(11)-C(12)	177(2)
			N(21)-C(21)-C(22)	180(1)

Table 10 Bond lengths (Å) and angles (degrees) for **309**.

Rh(1)-C(2')	2.005(5)	C(2')-C(3')	1.393(7)	Rh(1)-N(1)	2.051(4)
C(3')-C(4')	1.370(8)	Rh(1)-S(2)	2.227(1)	C(4')-C(5')	1.388(9)
Rh(1)-O(1)	2.234(3)	C(5')-C(6')	1.374(8)	Rh(1)-Cl(2)	2.346(1)
S(1)-O(1)	1.530(3)	Rh(1)-Cl(1)	2.355(1)	S(1)-C(11)	1.772(6)
N(1)-C(2)	1.341(7)	S(1)-C(12)	1.776(6)	N(1)-C(6)	1.352(7)
S(2)-O(2)	1.468(4)	C(2)-C(3)	1.374(8)	S(2)-C(22)	1.771(5)
C(2)-C(7)	1.502(8)	S(2)-C(21)	1.777(6)	C(3)-C(4)	1.361(8)
C(1S)-Cl(3)	1.70(1)	C(4)-C(5)	1.380(8)	C(1S)-Cl(5)	1.74(1)
C(5)-C(6)	1.363(8)	C(1S)-Cl(4)	1.735(12)	C(7)-O(7)	1.225(6)
S(3)-O(3)	1.48(1)	C(7)-C(1')	1.469(8)	S(3)-C(31)	1.54(3)
C(1')-C(2')	1.398(7)	S(3)-C(32)	1.72(2)	C(1')-C(6')	1.40(1)

C(2')-Rh(1)-N(1)	89.6(2)	C(1')-C(7)-C(2)	121.3(5)
C(2')-Rh(1)-S(2)	89.0(2)	C(2')-C(1')-C(6')	119.5(5)
N(1)-Rh(1)-S(2)	92.5(1)	C(2')-C(1')-C(7)	124.1(5)
C(2')-Rh(1)-O(1)	179.0(2)	C(6')-C(1')-C(7)	116.4(5)
N(1)-Rh(1)-O(1)	89.6(2)	C(3')-C(2')-C(1')	118.2(5)
S(2)-Rh(1)-O(1)	90.5(1)	C(3')-C(2')-Rh(1)	119.0(4)
C(2')-Rh(1)-Cl(2)	94.8(2)	C(1')-C(2')-Rh(1)	122.6(4)
N(1)-Rh(1)-Cl(2)	175.6(1)	C(4')-C(3')-C(2')	121.5(5)
S(2)-Rh(1)-Cl(2)	87.30(5)	C(3')-C(4')-C(5')	120.6(5)
O(1)-Rh(1)-Cl(2)	86.0(1)	C(6')-C(5')-C(4')	118.7(5)
C(2')-Rh(1)-Cl(1)	90.6(2)	C(5')-C(6')-C(1')	121.4(6)
N(1)-Rh(1)-Cl(1)	88.2(1)	O(1)-S(1)-C(11)	103.6(2)
S(2)-Rh(1)-Cl(1)	179.20(5)	O(1)-S(1)-C(12)	105.3(2)
O(1)-Rh(1)-Cl(1)	90.0(1)	C(11)-S(1)-C(12)	97.6(3)
Cl(2)-Rh(1)-Cl(1)	92.11(5)	S(1)-O(1)-Rh(1)	118.7(2)
C(2)-N(1)-C(6)	118.4(5)	O(2)-S(2)-C(22)	108.7(3)
C(2)-N(1)-Rh(1)	126.1(4)	O(2)-S(2)-C(21)	107.3(3)
C(6)-N(1)-Rh(1)	115.4(3)	C(22)-S(2)-C(21)	100.9(3)
N(1)-C(2)-C(3)	121.6(5)	O(2)-S(2)-Rh(1)	115.2(2)
N(1)-C(2)-C(7)	120.7(5)	C(22)-S(2)-Rh(1)	110.8(2)
C(3)-C(2)-C(7)	117.5(5)	C(21)-S(2)-Rh(1)	113.0(2)
C(4)-C(3)-C(2)	120.0(5)	Cl(3)-C(1S)-Cl(5)	115.2(8)
C(3)-C(4)-C(5)	118.5(5)	Cl(3)-C(1S)-Cl(4)	112.2(7)
C(6)-C(5)-C(4)	119.6(5)	Cl(5)-C(1S)-Cl(4)	113.0(7)
N(1)-C(6)-C(5)	121.8(5)	O(3)-S(3)-C(31)	106(1)
O(7)-C(7)-C(1')	120.7(5)	O(3)-S(3)-C(32)	110(1)
O(7)-C(7)-C(2)	117.3(5)	C(31)-S(3)-C(32)	107(2)

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